

TOPICAL REVIEW

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**Topical Review**

# Review on chemical mechanical polishing for atomic surfaces using advanced rare earth abrasives

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**Abstract**

During the past decades, high-performance devices and setups have been widely used in the fields of precision optics, semiconductors, microelectronics, biomedicine, optoelectronics and aerospace. It is a challenge to achieve ultralow surface roughness free of damages. Due to the unique physicochemical properties of rare earths, ceria has garnered great progresses for atomic surfaces induced by chemical mechanical polishing. Compared with conventional mechanical removal by alumina and silica, rare earth abrasives achieve selective material removal on surface via their special chemical activity, without introducing microscopic scratches and defects. Nevertheless, polishing performance of rare earth abrasives depends on series of factors, e.g. size of abrasive particles, microscale topological structure, configuration of chemical slurry, auxiliary energy fields etc. As a result, it is significant to conduct a comprehensive review to understand state-of-the-art polishing technologies. This review summarizes the effect of polishing slurries composed of different rare earth abrasives on polishing performance under different conditions. Additionally, various energy-assisted

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polishing strategies are discussed using diverse kinds of rare earth abrasives for distinct polishing forms. Finally, future directions of polishing on rare earth abrasives are addressed.

**Keywords:** rare earth abrasives, chemical mechanical polishing, performance, energy field-assisted polishing, atomic surface

## 1. Introduction

Rare earth elements have been widely applied to metallurgy, petrochemical, optical fiber communication, ultra-precision machining, optoelectronics, microelectronics and aerospace industries, because of their particular physical and chemical properties [1–4]. They can be easily ionized to form trivalent stable ions, in which lanthanum, cerium and europium are the most active [5]. Stable compounds of rare earths form with oxygen, hydrogen, ammonia, sulfur, nitrogen, carbon, and other halogens [6]. Moreover, rare earths can also generate disparate metal compound alloys. Due to these peculiar characteristics, rare earths have been found great applications in chemical mechanical polishing (CMP) [7, 8].

With development of ultra-precision polishing technology [9, 10], demands for ultra-smooth, ultralow-damage surfaces are becoming increasingly apparent. During 1920s, rare earth abrasives were used to polish gun sights of antiaircraft. To date, ultra-precision optics [11], semiconductor processing [12], precision medical care [13], inertial navigation [14] for higher demands on surface quality of high-performance products [15, 16]. Under this background, CMP using rare earth oxide abrasives (mainly CeO<sub>2</sub>) has emerged [17]. Rare earth oxide abrasives exhibit advantages in advanced polishing surface quality, high polishing efficiency, long polishing life, low cost and easy to clean [18, 19], compared to those of traditional abrasives. Nowadays, sizes of ceria varied from  $\mu\text{m}$  to nm have been prepared to meet the industrial and research demands, mainly through solid and liquid phase reaction methods [20].

In the past few decades, rare earth abrasives, such as ceria, have made a profound influence on ultra-precision polishing, and the angstrom surfaces ( $<0.2\text{ nm}$ ) are efficiently achieved [21]. Although the polishing powder has the above excellent performances, it is still unable to meet the processing needs of modern ultra-precision optical components with complex structures. Especially, advanced technologies such as photo-masks and projection lenses in photolithography machines [22–24], fusion and laser weapons lens [25–27], ultra-high quality factor optical microcavity [28–30] all require the use of optical glass with atomic-level surface quality. Consequently, series of work has been conducted to further improve the polishing efficiency and precision. In this regard, diverse polishing technologies are developed, including abrasives, slurries with different components, and energy field assisted polishing technologies [31, 32]. In fact, polishing performance is directly related to topology structure, composite components,

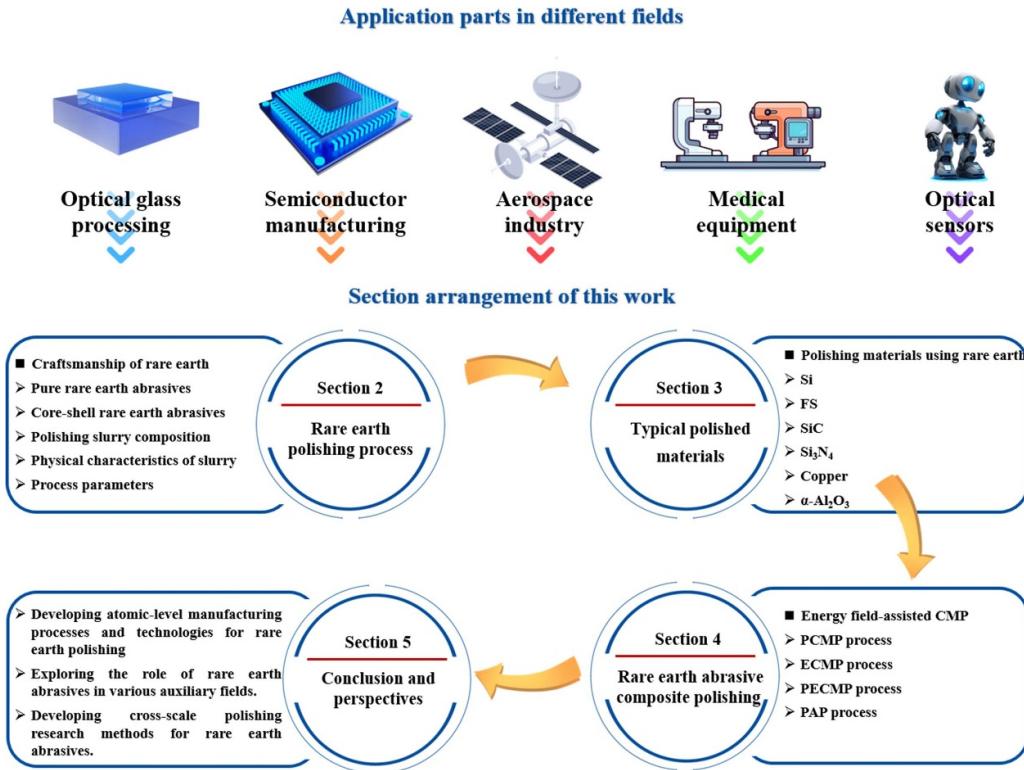
and size of abrasives, as well as slurry composition, specific polishing process and parameters [33]. These works have importantly promoted the development of CMP with rare earth abrasives. Nonetheless, previous researches on CMP using rare earth abrasives have not yet been systematically summarized and discussed.

In this work, recent advancements in CMP are reviewed over the past two decades based on ceria mainly, consisting of development of rare earth abrasives, slurry and advanced composite polishing processes. Meanwhile, the challenges of current research and future directions of CMP with rare earth abrasives are presented. Structure of this review is presented and organized in figure 1. In section 2, the influence of different polishing slurry compositions for macro polishing performance are evaluated, including abrasive types, pH regulators, oxidizer and other additives. In terms of section 3, polishing mechanism of different typical polished materials are explored, mainly contains Si, SiO<sub>2</sub>, SiC, Si<sub>3</sub>N<sub>4</sub> and so on. While in section 4, different energy field assisted polishing devices are discussed and compared. Finally, the section 5 summarizes the current status of rare earth abrasives and provides an outlook on their development prospects in CMP.

## 2. Research on polishing process

### 2.1. Polishing abrasives

In general, the use of abrasives, by means of physical actions such as friction and abrasion, facilitates the elimination of surface irregularities, protrusions, and defects. This process is crucial for the removal of films, oxide layers, or other surface coatings in order to achieve optimal surface planarization [34]. Conventional polishing abrasives, such as Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, are typically employed through mechanical friction on the material surface due to their higher hardness compared to rare earth abrasives, aiming to achieve material removal [35]. However, this may result in the introduction of microscopic scratches or surface damage during the polishing process, constraining the formation of the ultimate ultra-precision surface. In contrast, rare earth abrasives utilize unique chemical activity to selectively remove material from the surface, finding widespread application in ultra-precision surface machining. The selection and control of polishing abrasives are paramount to ensuring the desired surface planarity during the CMP process [36, 37]. Different types of abrasives can yield different polishing effects. This chapter primarily focuses on rare earth abrasives used in CMP.



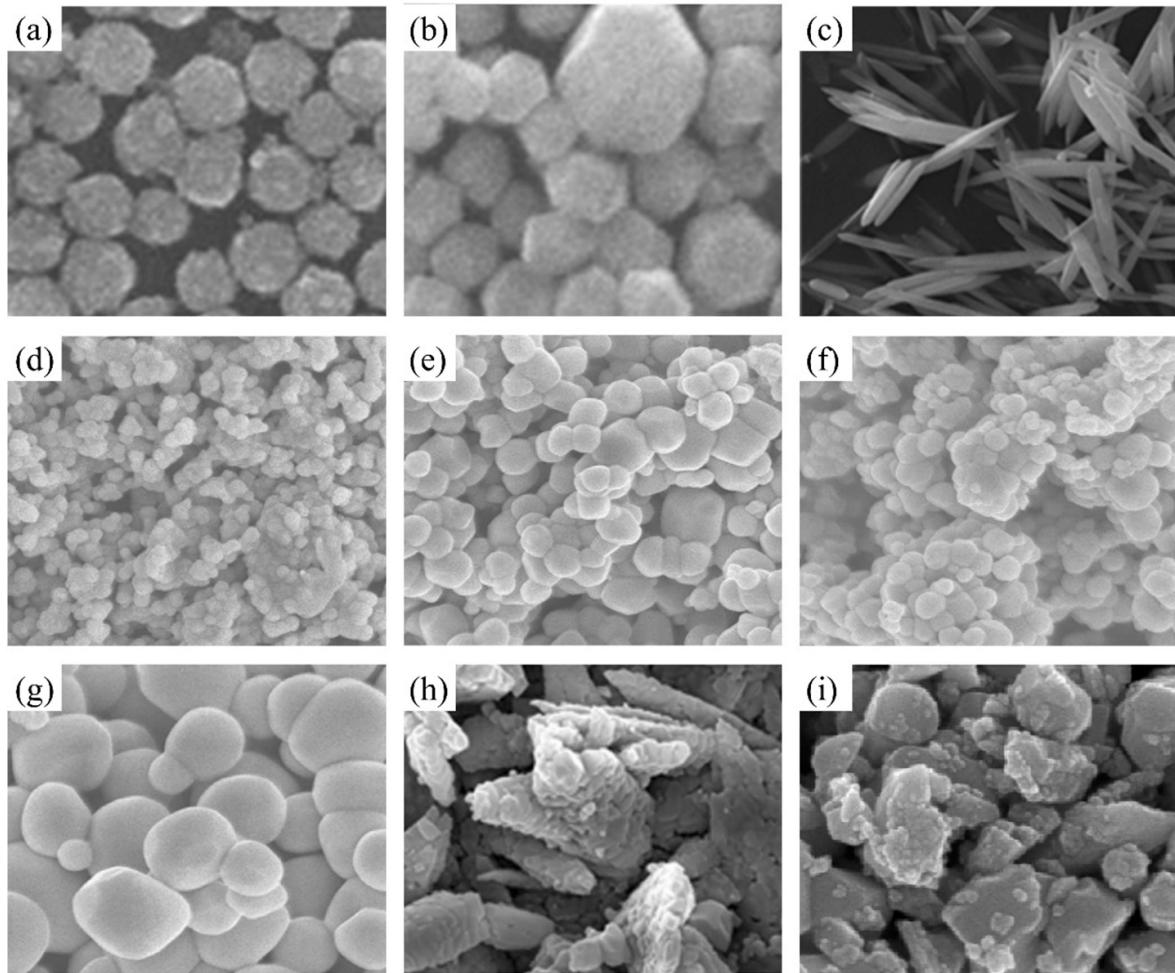
**Figure 1.** Structure of this review paper and the application of rare earth abrasives in various areas.

**2.1.1. Pure rare earth abrasives.** Pure rare earth abrasives mainly refer to pure rare earth abrasives and pure rare earth abrasives doped with other elements, typically obtained through processes such as smelting, chemical synthesis, or purification. In CMP, chemically synthesized methods, such as the precipitation method [38], sol–gel method [39], homogenous precipitation [40], urea condensation [41], co-precipitation method, and hydrothermal synthesis are commonly selected for pure rare earth abrasives. The scanning electron microscopy (SEM) images in figure 2 illustrate the morphological characteristics of the novel pure rare earth abrasives. It can be observed that rare earth abrasives come in various shapes, including circular, polygonal, rod-like forms etc. The nanoclustered and highly crystalline cerium oxide nanoparticles (NPs), as shown in figures 2(a) and (b), presenting circular and polygonal shapes. Studies indicate that nanoclustered NPs in circular shape exhibit low crystallinity and a high Ce<sup>3+</sup>/Ce<sup>4+</sup> ratio [42]. Ho *et al* developed a new spindle-like CeO<sub>2</sub> in figure 2(c), the band gap energy of the sample was determined by Ultraviolet–Vis spectroscopy as rod-shaped > spherical > spindle-like [43]. The particles prepared from different cerium precursors are shown in figures 2(d)–(g), and the comparison reveals that particles prepared from oxides exhibit better uniformity in cerium oxide particle distribution [44]. The CeO<sub>2</sub> NPs (figure 2(h)) synthesized with urea condensation by Wang *et al* exhibit excellent monodispersity [41]. Lim *et al* studied the influence of CeO<sub>2</sub> abrasive particle (figure 2(i)) size on the height of oxide steps and the amount of dishing [45]. In general, different shapes of CeO<sub>2</sub> abrasive are suitable for various machining needs

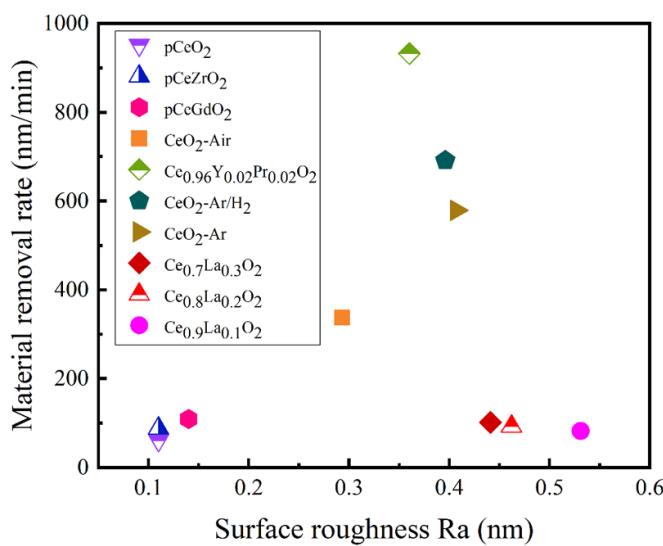
and workpiece characteristics. Rod-shaped abrasives typically have sharper edges, providing a certain directional effect during machining, aiding in controlling the grinding path and direction, allowing for finer grinding in local areas. Polygonal abrasives have multiple grinding surfaces, enabling simultaneous grinding in different directions, better adapting to the curvature and angles of the workpiece surface, improving machining efficiency. Flat abrasives are particularly advantageous for machining flat surfaces due to their enhanced controllability, which minimizes errors and enhances machining precision. Spherical abrasives with smooth surfaces and no sharp edges tend to produce fewer scratches and obtain higher surface quality on material surface, and it is possible to obtain atomic surface [46].

Moreover, the effectiveness of ceria abrasives can be boosted by doping elements like Y, La and Zr. Ultra-smooth surface can be obtained after polishing with appropriate CeO<sub>2</sub> abrasive [47]. The surface roughness Ra (within  $5 \times 5 \mu\text{m}^2$ ) and material removal rate (MRR) of SiO<sub>2</sub> after polishing with CeO<sub>2</sub>, porous ceria (pCeO<sub>2</sub>), Zr-doped pCeO<sub>2</sub> (pCeZrO<sub>2</sub>), Gd-doped pCeO<sub>2</sub> (pCeGdO<sub>2</sub>) [48], CeO<sub>2</sub>-Air, CeO<sub>2</sub>-Ar, CeO<sub>2</sub>-Ar/H<sub>2</sub> [49], Ce<sub>0.9</sub>La<sub>0.1</sub>O<sub>2</sub>, Ce<sub>0.8</sub>La<sub>0.2</sub>O<sub>2</sub>, Ce<sub>0.7</sub>La<sub>0.3</sub>O<sub>2</sub> [50], Ce<sub>0.96</sub>Y<sub>0.02</sub>Pr<sub>0.02</sub>O<sub>2</sub> [19] abrasives are shown in figure 3. It can be observed that using porous ceria for polishing SiO<sub>2</sub> yields a smoother surface. Ceria doped with La exhibits the highest Ra and MRR. Moreover, ceria synthesized in a reducing gas environment demonstrates superior polishing performance compared to ceria synthesized in air.

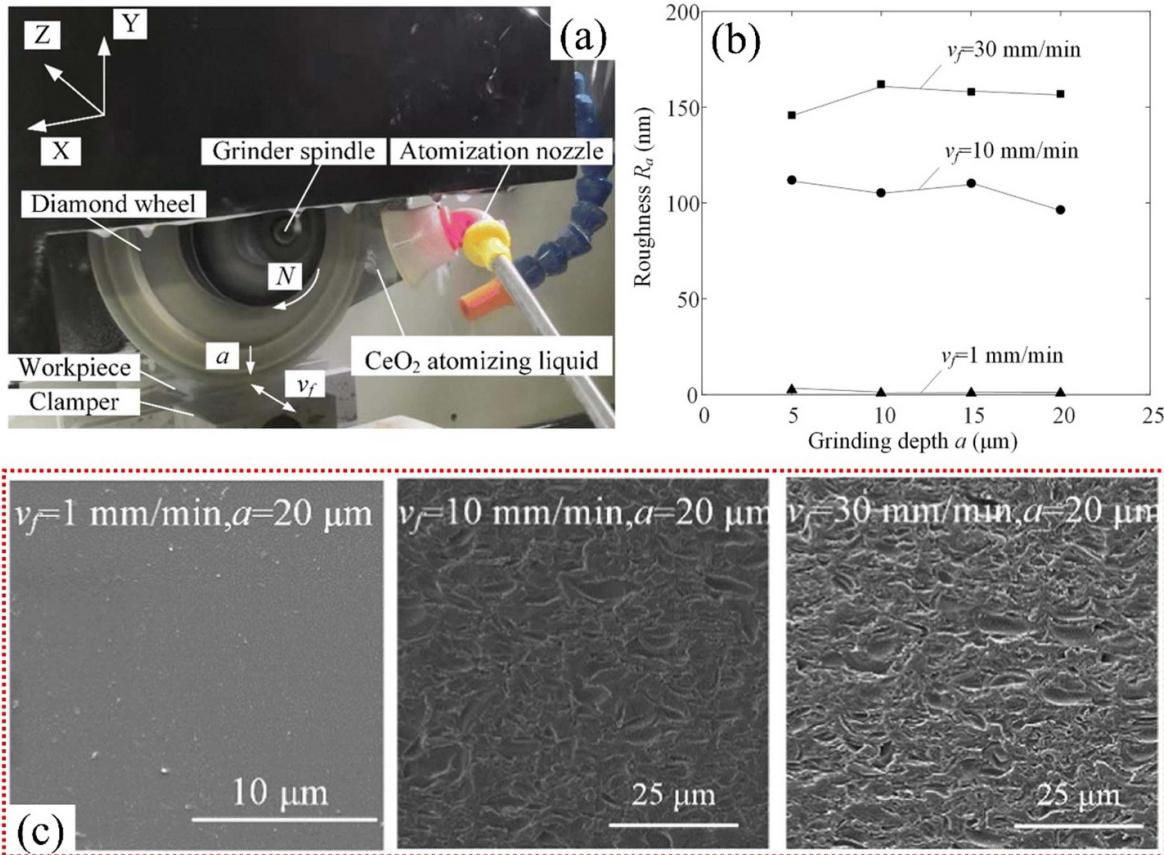
Abrasive size is another factor that have huge impact on the polished surface roughness. Among them, using smaller



**Figure 2.** SEM images of pure rare earth abrasives with different structures: (a) Nanoclustered ceria abrasive. (b) Highly crystalline ceria abrasive. (c) Spindle-like CeO<sub>2</sub> abrasive. (d) Ce(OH)<sub>4</sub> abrasive. (e) CeN abrasive. (f) CeCl<sub>3</sub> abrasive. (g) Irregular elliptical-shape CeO<sub>2</sub> abrasive. (h) A strip CeO<sub>2</sub> abrasive combination. (i) Polygonal-shaped CeO<sub>2</sub> abrasive. (a), (b) Reproduced from [42], with permission from Springer Nature. (c) Reprinted with permission from [43]. Copyright (2005) American Chemical Society. (d)–(g) Reprinted from [44], Copyright (2011), with permission from Elsevier. (h) Reproduced from [41], with permission from Springer Nature. (i) Reprinted from [45], Copyright (2005), with permission from Elsevier.



**Figure 3.** Material removal rate-surface roughness data of different types of pure rare earth abrasives.



**Figure 4.** (a) The experimental scene schematic of axis-feed grinding. (b) Surface roughness obtained at different feed rates and grinding depths. (c) Surface morphology obtained at different feed rates and grinding depths. (a)–(c) Reproduced from [56], with permission from Springer Nature.

abrasives tends to result in a higher edge removal rate compared to using larger abrasives [51, 52]. Therefore, during the polishing process, larger-sized abrasives can be initially used to achieve a certain surface precision in the shortest possible time, and then smaller-sized abrasives can be employed to polish the material surface to achieve a level of smoothness close to atomic-level cleanliness [53].

Essentially, rare earth abrasives exist not only in powder form but also in a gel (hydrosol) state [54, 55]. Nano cerium dioxide sol can be synthesized through the sol-gel process. Kim *et al* utilized two colloidal ceria abrasives, NC-ceria and CF-ceria, for polishing SiO<sub>2</sub> [42]. Verified through experimental analysis, nanocluster ceria abrasives possess both physical pliancy and chemical reactivity, exhibiting outstanding SiO<sub>2</sub> removal capability. The MRR is 890.4 nm min<sup>-1</sup>, showing significant potential for scratch inhibition in CMP processing.

Noticed that the pure ceria abrasives are already capable for generating atomic surface roughness. The core mechanism for doping different elements in the ceria abrasives is to increase the concentration of Ce<sup>3+</sup>. As a result, the oxygen vacancy in the abrasives increases which can greatly promote the MRR. Another breakthrough of application would be the addition of ceria into the grinding fluid, which cleverly introduces the polishing mechanism into grinding of hard brittle materials

to obtain better surface roughness and lower surface damage. Zhang *et al* introduced a novel axis-feed grinding approach, assisted by pure CeO<sub>2</sub> atomizing liquid [56]. The experimental scene in figure 4(a). This approach employed relatively large-grain diamond grinding wheels and substantial grinding depth to achieve a nearly polished surface roughness. Ultimately, as shown in figures 4(b) and (c), at a feed rate of 1 mm min<sup>-1</sup> and a grinding depth of 20  $\mu\text{m}$ , the optimal roughness was 1.05 nm, which was originally believed not possible for grinding on such low precision grinding machine using pure water for cooling. The near polished surface roughness is a solid proof for the effectiveness of ceria abrasives in lowering fracture rate and promote surface quality.

**2.1.2. Core-shell rare earth abrasives.** For decades, composite abrasives have been widely used in CMP. Among the various types of abrasives available, CeO<sub>2</sub>-based NPs have gained significant popularity and are extensively employed in traditional CMP applications. These NPs are particularly effective in removing silica materials due to their well-established chemical-tooth action. Several cost-effective methods for synthesizing core-shell abrasives, including ceria are solvo-thermal approach, sol-gel technique, self-assembly process, electrochemical synthesis, and micro-emulsion

**Table 1.** Core–shell rare earth abrasives summary.

Abrasives	Polished material	Ra (nm)	MRR (nm/min)	Measuring range ( $\mu\text{m} \times \mu\text{m}$ )	References
PS/PANI/CeO <sub>2</sub>	SiO <sub>2</sub>	0.122	81		[64]
PMMA/CeO <sub>2</sub>	SiO <sub>2</sub>	0.154	266.2		[65]
mSiO <sub>2</sub> @CdS@CeO <sub>2</sub>	SiO <sub>2</sub>	0.134	NA		[66]
mSiO <sub>2</sub> @CeGdO <sub>2</sub>	SiO <sub>2</sub>	0.137	NA		[67]
Cs/CeO <sub>2</sub>	SiO <sub>2</sub>	0.11	93–127		[68]
Cs/CeYO <sub>2</sub>		0.10	128–150		[68]
mSiO <sub>2</sub> /CeO <sub>2</sub>	SiO <sub>2</sub>	NA	38–66		[69]
mSiO <sub>2</sub> /Ce <sub>0.83</sub> Er <sub>0.17</sub> O <sub>2</sub>		NA	71–99		
PS/CeO <sub>2</sub>	SiO <sub>2</sub>	0.11	26	5 × 5	[70]
D-mSiO <sub>2</sub> /CeO <sub>2</sub>		0.15	85		
Ce <sub>0.92</sub> La <sub>0.08</sub> O <sub>2</sub>	SiO <sub>2</sub>	0.648	562.66		[71]
Ce <sub>0.92</sub> Pr <sub>0.08</sub> O <sub>2</sub>		0.628	578.74		
Ce <sub>0.92</sub> Y <sub>0.08</sub> O <sub>2</sub>		0.509	626.97		
SiO <sub>2</sub> /CeO <sub>2</sub>	Si-Face 6 H-SiC	0.216	20.12		[72]
PS@CeO <sub>2</sub> :La	UTG	0.32	480.22		[73]
PS@CeO <sub>2</sub> /DND	Sapphire wafer	0.52	23.33–28.33		[74]
Polyurethane-CeO <sub>2</sub>	SiC	0.51	50–66.67	720 × 540	[75]
CeO <sub>2</sub> –TiO <sub>2</sub>	RB-SiC	1.112	9.817		[32]
PS/CeO <sub>2</sub>		0.589	14.633	2.5 × 2.5	
PS/CeO <sub>2</sub> –TiO <sub>2</sub>		0.497	20.383		

NA (Not available).

PS/PANI/CeO<sub>2</sub> (Polystyrene/Polyaniline/Ceria).

PMMA/CeO<sub>2</sub> (Polymethylmethacrylate/Ceria).

method [57]. There are also some polishing abrasives specifically designed for magnetic field-assisted polishing, with a removal rate significantly higher than traditional abrasives.

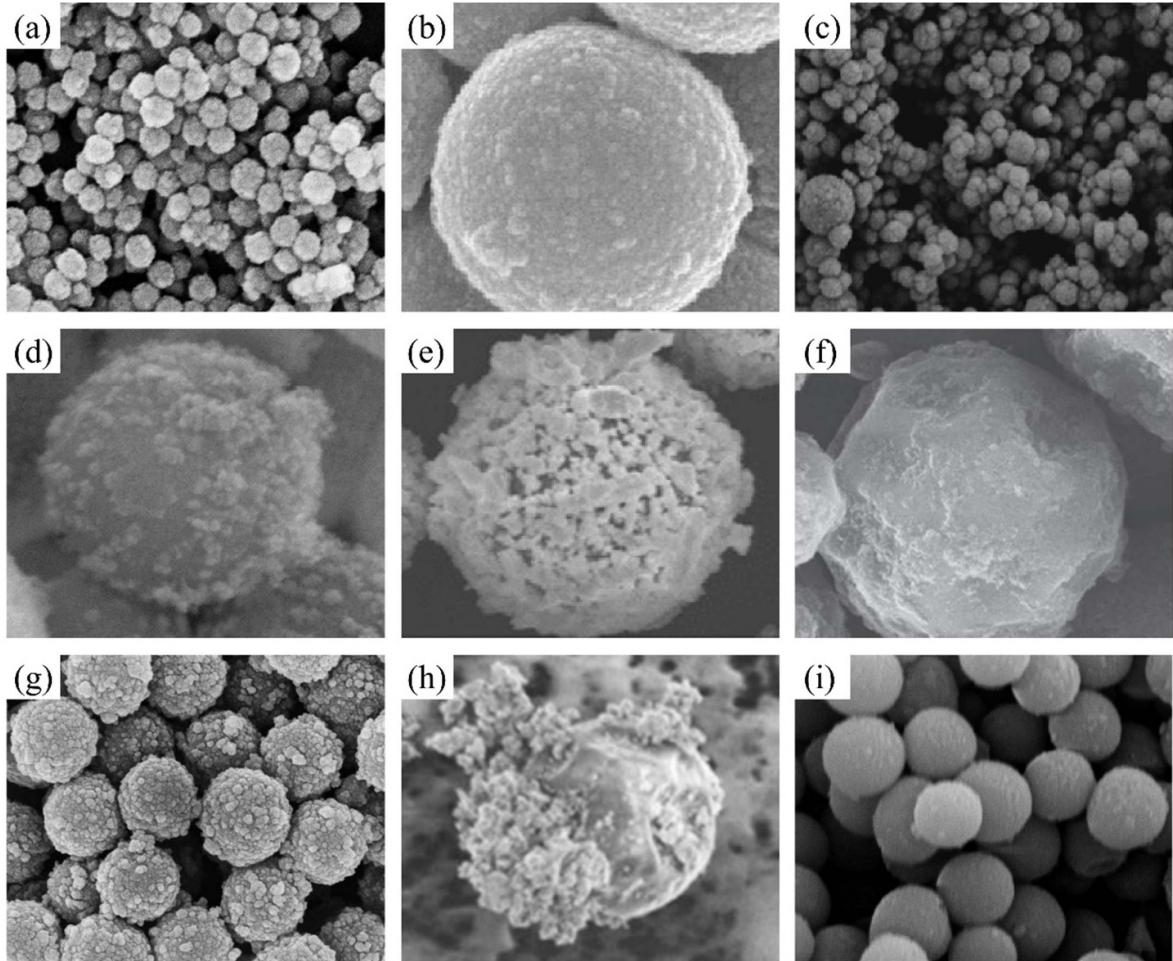
It is widely recognized that the polishing characteristics of CeO<sub>2</sub> abrasives are greatly influenced by factors such as size, shape, structure, component composition, and surface defects (Vo and Ce<sup>3+</sup>) at the nanoscale. To date, various types of CeO<sub>2</sub>-involved abrasives including core–shell structured [58], porous [42], metal-doped [59], non-spherical [60, 61], hybrid or mixed [62, 63]. Multiple novel polishing abrasives have been synthesized to enhance material surface quality and removal efficiency in CMP practice. A summary of Ra and MRR data obtained using core–shell rare earth abrasives on different materials can be found in table 1.

Numerous investigations have already been conducted on the synthesis and polishing effects of rare earth composite abrasives. The shape and function of abrasives synthesized through different methods vary, leading to differing effects on material surface quality and removal. Figure 5 illustrates the morphology of several different rare earth abrasives, and it can be observed that their shapes are varied. A three-step strategy is employed to construct hybrids of mSiO<sub>2</sub>@CdS@CeO<sub>2</sub> abrasives in figure 5(a), featuring mesoporous cores and double-layered core–shell heterostructures. The formation of the CdS-CeO<sub>2</sub> heterojunction facilitates efficient separation of photogenerated charge carriers and high activity oxygen production, bolstering the formation of photochemically reacted layers [66]. The core–shell structured PS@CeO<sub>2</sub>:La abrasives as shown in figure 5(b), the discovery indicates that La<sup>3+</sup> has a more pronounced modulation effect on lattice distortion and Ce<sup>3+</sup>/Ce<sup>4+</sup> chemical shift [73]. Figure 5(c) depicts CS/CeYO<sub>2</sub> core–shell abrasives, which

effectively enhance the removal rate [68]. The ternary composite abrasive PS@CeO<sub>2</sub>/DND (figure 5(d)) increases the polishing interface area under the joint action of the three components [74]. Under the influence of a strong electric field between electrodes, polyurethane (PU)-CeO<sub>2</sub>) core–shell abrasives (figure 5(e)) exhibit durability [75]. Compared to figure 5(f), the abrasive shown in figure 5(h) adheres CeO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub> abrasives unevenly to the polymer abrasives at a lower temperature of about 80 °C. Under the action of a magnetic field, the removal rate of this abrasive is significantly higher than that of conventional abrasives [76]. Chen *et al* developed various composite abrasives, PMMA/CeO<sub>2</sub> hybrid abrasives (figure 5(g)) can be used to produce polishing pads [65], mSiO<sub>2</sub>@CeGdO<sub>2</sub> (figure 5(i)) abrasives can significantly enhance the removal efficiency under ultraviolet light irradiation [67].

The monodispersity and morphology of abrasives are recognized as crucial factors influencing polishing rates [77–80]. The size and morphology of ceria abrasives can be regulated through the structure of ceria-coated silica nanoparticles [81]. It has been demonstrated that the slurry prepared using these nano-particles can enhance the selectivity between SiO<sub>2</sub> and SiN, thus increasing the selective removal rate [82]. Nevertheless, achieving monodispersity and morphology control for larger ceria abrasives remains a challenge due to the difficulty in controlling the particle growth of ceria [83].

The investigation revealed that the surface of CeO<sub>2</sub> abrasives throughout the polishing process contains not only Ce<sup>4+</sup> but also a certain amount of Ce<sup>3+</sup> [84]. Doping trivalent ions generates a significant number of oxygen vacancies [85], which promotes the formation of Ce<sup>3+</sup> on the CeO<sub>2</sub> crystal

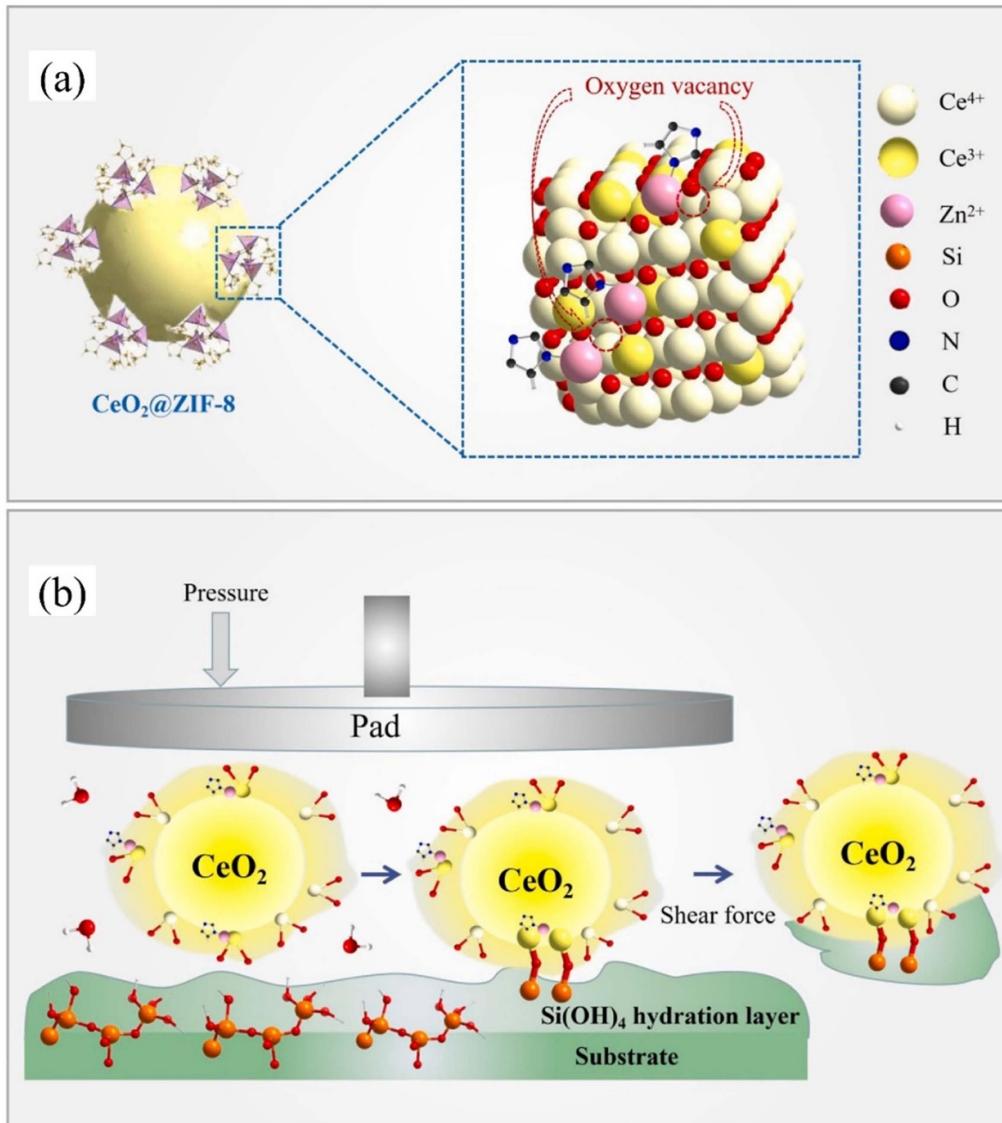


**Figure 5.** SEM images of composite rare earth abrasives. (a)  $\text{mSiO}_2@\text{CdS}@Ce\text{O}_2$  abrasive. (b)  $\text{PS}@Ce\text{O}_2:\text{La}$  abrasive. (c)  $\text{CS}/Ce\text{YO}_2$  abrasive. (d)  $\text{PS}@Ce\text{O}_2/\text{DND}$  abrasive. (e)  $\text{PU}-Ce\text{O}_2$  abrasive. (f)  $\text{Polymer}/Ce\text{O}_2-\text{Fe}_3\text{O}_4$  abrasive. (g)  $\text{PMMA}/Ce\text{O}_2$  hybrid abrasive. (h)  $\text{Polymer}/Ce\text{O}_2-\text{Fe}_3\text{O}_4$  abrasive. (i)  $\text{mSiO}_2@Ce\text{GdO}_2$  abrasive. (a): Reprinted from [66], Copyright (2023), with permission from Elsevier. (b): Reprinted from [73], Copyright (2023), with permission from Elsevier. (c): Reprinted from [68], Copyright (2022), with permission from Elsevier. (d): Reprinted from [74], Copyright (2021), with permission from Elsevier. (e): Reprinted from [75], Copyright (2017), with permission from Elsevier. (f) and (h): Reprinted from [76], Copyright (2016), with permission from Elsevier. (g): Reprinted from [65], Copyright (2015), with permission from Elsevier. (i): Reprinted from [67], Copyright (2023), with permission from Elsevier.

compared to other ions [86]. The bonding strength between ceria and  $\text{SiO}_2$ , along with the rate of ceria NPs attachment onto a  $\text{SiO}_2$  surface, exhibited an upward trend in correlation with the surface concentration of  $\text{Ce}^{3+}$ , improving polishing precision and achieving surfaces with precision and ultra-precision machining [87, 88]. Generally, experimental validation has confirmed that doping with  $\text{Ce}^{3+}$  enhances CMP performance of  $\text{CeO}_2$  abrasives, leading to modifications in their properties. However, additional research is necessary to gain a deeper comprehension of how various doping types and quantities affect the crystal structure, microscopic morphology, and presence of defects in  $\text{CeO}_2$  abrasives. Studies have demonstrated that doping with  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$ , and  $\text{Pr}^{3+}$  can significantly increase the concentration of  $\text{Ce}^{3+}$  on the surface of  $\text{CeO}_2$  abrasives [50].  $\text{Y}^{3+}$  doping is more favorable for the transition from  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  compared to  $\text{La}^{3+}$  and  $\text{Pr}^{3+}$  doping [71]. The introduction of dopants (La, Nd, and Yb) can promote the formation of oxygen vacancies in  $\text{CeO}_2$  and the transformation of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  [89]. Abrasives

with zeta potential dependency notably enhance MRR [90]. Yuan *et al* synthesized composite abrasives called  $\text{CeO}_2@ZIF-8$  [91]. The incorporation of ZIF-8 onto the surface of  $\text{CeO}_2$  promotes the creation of additional oxygen vacancies within the cerium lattice, as depicted in figure 6(a). Consequently, an increased number of  $\text{Ce}^{3+}$  ions become exposed on the surface of  $\text{CeO}_2@ZIF-8$  abrasives [92], leading to enhanced polishing performance. The principle of CMP on glass surface is illustrated in figure 6(b).

Based on above section, it can be seen that the lowest surface roughness is achieved by pure rare earth abrasives. The main purpose of fabricating composite rare earth abrasives is to achieve higher MRR utilizing the special mechanism between additives and the ceria. Doping of elements like Y, La, Pr and Nd are also frequently found on core–shell rare earth abrasives, which also serves the same purpose of increasing oxygen vacancy. Different mechanical or chemical properties of the core and the shell material are successfully coupled to combine the advantage of both materials. But the cost and the



**Figure 6.** (a) The space filling model of the  $\text{CeO}_2@\text{ZIF-8}$  surface structure. (b) Principle of polishing glass using  $\text{CeO}_2@\text{ZIF-8}$  abrasive. (a) and (b): Reprinted from [91], Copyright (2023), with permission from Elsevier.

fabrication complexity continue to hinder the grant application of core–shell abrasives in manufacturing. In the future, it would continuously be a hot topic for new fabrication and doping techniques.

## 2.2. Polishing slurry composition

In general, a polishing slurry consists of abrasives, the base solution, pH adjusters, dispersants, oxidizing agents, and other components [93, 94]. Each component serves distinct functions to ensure the slurry's excellent performance [95]. However, the majority of polishing slurries mentioned in the literature often consist of more than four components and involve the utilization of potent acids, alkalis, or hazardous chemicals. These slurries not only have the potential to corrode polishing equipment but also pose significant risks to both the

environment and operators. Furthermore, effectively removing any remaining surface attachments following the CMP process presents a formidable challenge [96, 97]. In contrast, the utilization of polishing slurries prepared with rare earth abrasives does not cause environmental pollution, achieving the effect of environmentally friendly and green polishing [21]. The summary of surface roughness and MRR values after polishing with different polishing slurries on different materials is listed in table 2.

**2.2.1. The dispersant.** In the polishing process, there are situations where it is inconvenient to use physical stirring for the polishing slurry. This leads to precipitation, aggregation, and stratification of the polishing slurry, causing variations in the composition of the polishing slurry used during the

**Table 2.** Typical rare earth abrasive polishing slurries composition.

Abrasives	Composition of polishing slurry	Polished material	Ra /Sa (nm)	MRR (nm/min)	Measuring range ( $\mu\text{m} \times \mu\text{m}$ )	References
CeO <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub> and DIW	SiO <sub>2</sub>	Sa = 0.093	125.34	20 × 20	[98]
CeO <sub>2</sub>	h-BN nanoflakes, KOL, and DIW	SiO <sub>2</sub>	Sa = 0.124	532	10 × 10	[99]
CeO <sub>2</sub>	LaOF, K <sub>4</sub> P <sub>2</sub> O <sub>7</sub> , SNLS, PAAS and DIW	SiO <sub>2</sub>	Sa = 0.23	530.52	50 × 50	[100]
CeO <sub>2</sub>	SA, SDS and DIW	SiO <sub>2</sub>	Sa = 0.08	553.58	20 × 20	[21]
Colloidal ceria	KMnO <sub>4</sub> at pH 2	6 H-SiC	Ra = 0.11	18.15	2 × 2	[101]
CeO <sub>2</sub>	(NaPO <sub>3</sub> ) <sub>6</sub> , CH <sub>3</sub> COOH	P-Si (100)	NA	412	NA	[102]
CeO <sub>2</sub>	DIW, acrylic	STI	NA	288.3	NA	[103]
CeO <sub>2</sub>	Corn oil, Na <sub>2</sub> CO <sub>3</sub> solution, and polysorbate	KDP	Sa = 0.648	644	100 × 100	[104]
CeO <sub>2</sub>	SiO <sub>2</sub> , H <sub>2</sub> O <sub>2</sub> , NaHCO <sub>3</sub> , Polyaspartic acid and DIW	Cu	Sa = 0.092	NA	50 × 50	[105]
SiO <sub>2</sub> /CeO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub> , GLY, BTA, NaOH	Cu	Ra = 0.363	279	5 × 5	[106]
CeO <sub>2</sub>	H <sub>2</sub> O, dilute hydrochloric acid	Lime glass	Sa = 1.56	365.5	500 × 500	[107]
CeO <sub>2</sub> –NH <sub>2</sub>			Sa = 1.53	370.33		
CeO <sub>2</sub> –EDTA			Sa = 1.31	490.5		

NA (Not available).

polishing process, thus failing to achieve the desired polishing effect. Therefore, it is necessary to add dispersant to the polishing slurry to maintain the dispersion of abrasives, prevent their agglomeration, ensure uniform distribution on the surface during polishing, and enhance the stability of the polishing slurry to prevent component stratification or precipitation, maintaining consistent polishing results.

Anionic dispersants help prevent the aggregation and accumulation of abrasives, maintaining the uniform dispersion of abrasives in the polishing slurry. In order to maintain the stability of polishing slurries, two types of anionic dispersants are commonly used, sodium N-lauroyl sarcosinate (SNLS) and sodium polyacrylate (PAAS). These dispersants ensure that the abrasives in the slurry have a more uniform particle size distribution, resulting in a smoother surface after polishing [100]. Additionally, organic acids such as acetic acid, propionic acid, lactic acid, and citric acid are frequently employed as dispersants in CMP [108]. The evaluation of dispersion stability reveals that using acetic acid with CeO<sub>2</sub> suspension leads to moderate particle size distribution, good stability (zeta potential >50 mV), monodispersity (polydispersity index <0.1), and higher chemical activity due to increased Ce<sup>3+</sup> content [109]. This ultimately results in a higher removal rate.

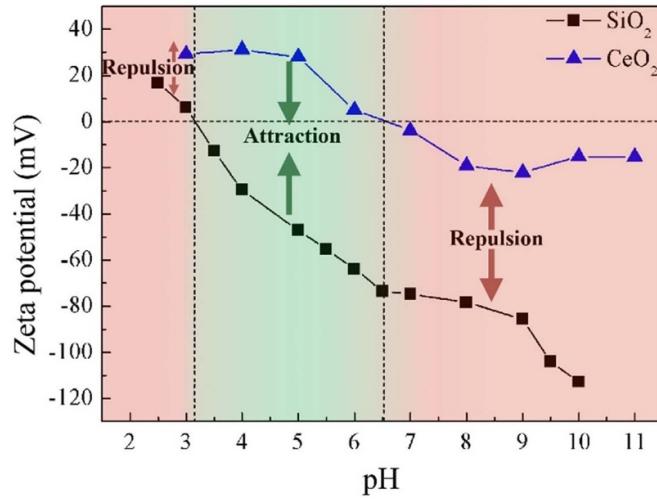
Various polymers with different functional groups can be introduced as non-ionic surfactants during the preparation process of CeO<sub>2</sub> slurry, including polyethylene glycol (PEG), polyacrylamide, polyvinylpyrrolidone (PVP-K30), polyvinyl alcohol (PVA-124), and polypropylene glycol [110]. The experiment indicates that elevated zeta potential values can improve particle dispersion when using deionized water-based slurries [111], and non-ionic surfactants with more C–O bonds exhibit stronger dispersing effects and greater adsorption

capacity on Si<sub>3</sub>N<sub>4</sub> surfaces. Therefore, selecting the appropriate dispersant is of crucial significance for enhancing the polishing effectiveness.

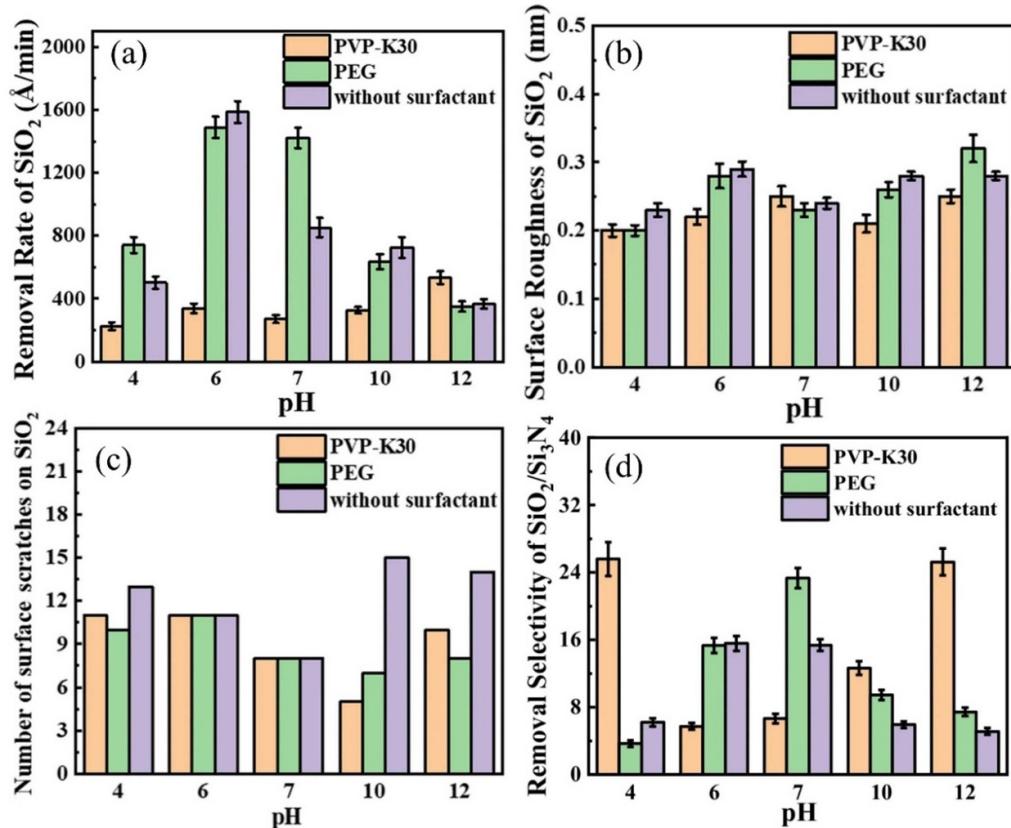
**2.2.2. pH regulators.** To comprehend the ceria-silica CMP mechanisms, certain researchers conducted an investigation on the influence of cerium slurry pH on the removal efficiency and surface morphology of silicon dioxide [112]. When adjusting the pH values using HCl and KOH, low removal rates of silica were observed in highly acidic conditions, with the maximum removal efficiency occurring when the pH reached 6.0 [113]. In conditions with pH ranging from neutral to alkaline, moderate rates of silica removal were observed. The acceleration in the removal rate beyond pH 9 can be attributed to an enhanced dissolution of silica. It is evident that the efficiency of ceria slurries in removing silica is greatly influenced by pH, reaching its maximum near the isoelectric point of the ceria slurry.

The electrostatic interactions between the abrasives and the wafer surface is significantly influenced by their individual zeta potentials [41]. When abrasives and wafer surfaces carry opposite charges, electrostatic attraction accelerates the polishing rate of the wafer material. Figure 7 compares the zeta potentials of pristine CeO<sub>2</sub> NPs and silicon dioxide surfaces [89]. When the pH of the slurry exceeds 6.5 or falls below 3.2, electrostatic repulsion occurs, resulting in a slower polishing rate. Conversely, when the pH of the slurry is within the range of 3.2–6.5, electrostatic attraction occurs, leading to an accelerated polishing rate. This explains why the MRR of SiO<sub>2</sub> is higher in acidic slurries than in alkaline slurries.

Several studies have been conducted to investigate the impact of different non-ionic surfactants in CeO<sub>2</sub>-based slurries at varying pH values on MRR, selectivity of removal, and surface quality during wafer polishing. The experimental



**Figure 7.** Zeta potential curve of pristine  $\text{CeO}_2$  nanoparticles and silica surface changed with slurry pH. Reprinted from [89], Copyright (2020), with permission from Elsevier.



**Figure 8.** (a) Removal rate, (b) surface roughness, (c) surface scratches count of  $\text{SiO}_2$ , and (d) removal selectivity between  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  after  $\text{CeO}_2$  slurries polished with/without PVP-K30 and PEG at different pH values. (a)–(d): Reprinted from [110], Copyright (2023), with permission from Elsevier.

results demonstrate that at pH values of 4, 6, 7, and 10, non-ionic surfactant polyethylpyrrolidone (PVP-K30) exhibits a stronger inhibitory effect on  $\text{SiO}_2$  MRR compared to PEG (figure 8(a)) [110]. The reason for this is due to the smaller zeta potential of the PVP-K30 mixed suspension with  $\text{CeO}_2$  compared to that of the PEG mixed suspension, resulting in a more

powerful repulsion between the suspension and  $\text{SiO}_2$ . PVP-K30 demonstrates selective removal properties in both acidic and alkaline environments, while PEG shows significant removal effectiveness in neutral pH environments (figure 8(b)). The surface roughness of  $\text{SiO}_2$  polished with  $\text{CeO}_2$  slurries containing either PVP-K30 or PEG remains between 0.20 nm and

0.32 nm (figure 8(c)). Moreover, the addition of PVP-K30 and PEG reduces the number of scratches on the polished  $\text{SiO}_2$  surface, with fewer scratches observed in alkaline environments compared to acidic ones (figure 8(d)).

**2.2.3. The oxidizer.** In the polishing slurry, the incorporation of an oxidizing agent serves to oxidize the material layer, generating a pliable and active oxide film on the surface, aiding in material removal. The corrosion rate is significantly influenced by the type and concentration of the oxidant. When the oxidation potential or concentration is low, the fraction of the reacted surface is low, leading to hard contact between the abrasives and the surface and more surface defects. Conversely, a compact and rigid oxide layer may develop, impeding subsequent mechanical removal. Hence, varying oxidizer types or adjusting concentrations is imperative for different materials [114]. The commonly used oxidizer primarily include hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) [115], ozone ( $\text{O}_3$ ),  $\text{KMnO}_4$ ,  $\text{K}_2\text{S}_2\text{O}_8$  [116–118],  $\text{K}_2\text{FeO}_4$ ,  $\text{Fe}(\text{NO}_3)_3$  [119],  $\text{KIO}_3$  [120],  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , sodium percarbonate [121], Oxone [122–124], citric acid, corrosion inhibitor (BTA) [125], Fenton reagent and other persulfates. Among them, the order of influence on MRR, from high to low, is as follows: persulfates, peroxides, potassium permanganate, peroxodisulfates,  $\text{O}_3$ , hydrogen peroxide, and so on [126–128]. However, based on the result form previous study, hydrogen peroxide is preferable since it forms harmless decomposition and by-products in the reaction. It is also revealed that in photo CMP (PCMP), the introduction of ultraviolet light can effectively generate oxidation agents like  $\text{O}_3$ , which is another approach for introducing oxidizer without worrying of distribution and oxidants stabilization [129].

**2.2.4. Mixed additives.** Mixed additives refer to the addition of various substances during the preparation of the polishing slurry to enhance its stability and polishing performance, aiming to achieve a high precision surface finish. Commonly used additives include pyridine hydrochloride, piperazine, imidazole, proline, arginine, glutamic acid, and pyridine carboxylic acid [130]. The results indicate that additives adsorb onto the surface of cerium oxide abrasives, affecting the interaction between the abrasive and silicon, thereby influencing the removal rate.

Research has indicated that after the addition of surfactants to ceria slurry, such as, poly-acrylic-acid, PEG, Sodium Dodecyl Benzene Sulfonate, Nonylphenol Ethoxylate, Cetyltrimethylammonium Bromide, the removal rate decreases with an increase in the concentration of surface-active agents [131]. According to Stokes' law of resistance [132], it can be inferred that a significant adsorption phenomenon occurring on the membrane surface leads to an elevation in local viscosity proximal to the surface. Consequently, this resultant layer functions as a protective barrier, impeding the approach of abrasive substances towards the membrane surface. Liu *et al* achieved a synergistic effect by incorporating hexagonal boron nitride (h-BN) as a lubricant with  $\text{CeO}_2$  abrasives, enhancing the lubricity and flowability of the slurry

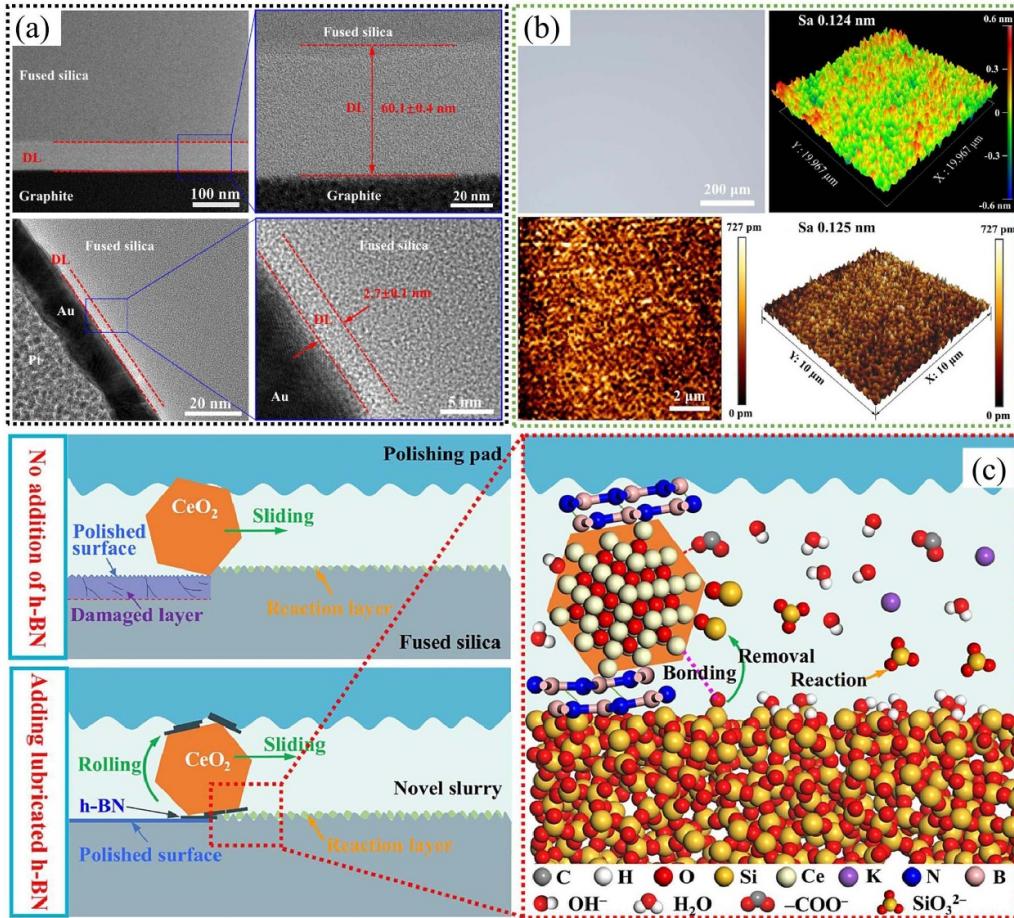
[99]. As shown in figures 9(a) and (b), the subsurface damage layer of fused silica (FS) reduces after CMP. The surface roughness is only 0.124 nm. Figure 9(c) demonstrates that with the assistance of the lubricant h-BN, the movement of  $\text{CeO}_2$  abrasives shifts from sliding to rolling, preventing excessive surface abrasion caused by irregularly shaped  $\text{CeO}_2$  abrasives. This significantly reduces subsurface damage and greatly decreases surface roughness. In conclusion, the addition of additives aids in optimizing the removal mechanism, enhancing MRR and Ra, reducing the subsurface damage layer, and achieving a smooth, defect-free surface, meeting the requirements of ultra-precision manufacturing processes.

### 2.3. Physical characteristics of slurry

The flow rate, temperature, viscosity, and concentration of abrasives in the polishing slurry all affect the polishing results. A low slurry flow rate (SFR) can result in a high polishing temperature [133], aggregation of abrasives, leading to defects such as scratches and marks on the material surface after polishing. A high SFR reduces the polishing temperature, lowers the chemical removal rate, increases the mechanical removal rate, enabling quick material removal, but excessive flow rates may make it difficult to control the polishing depth, leading to potential over-polishing or uneven processing [134]. As the polishing slurry temperature increases, abrasives aggregate [3], friction coefficient of metal materials increases, MRR increases [135], but surface roughness also increases. For silicon dioxide ( $\text{SiO}_2$ ), with increasing polishing slurry temperature, the particle size of  $\text{SiO}_2$  abrasives decreases, zeta potential becomes more negative, resulting in a smoother silica surface [136]. Generally, with increasing slurry viscosity, MRR increases [137–139], but flowability of abrasives worsens, making the material surface more prone to scratching during polishing [140]. Lowering abrasive concentration improves the surface flatness of the CMP slurry [141]. When polishing  $\text{SiO}_2$  with  $\text{CeO}_2$  abrasive, the MRR decreases with increasing abrasive concentration due to the adsorption of  $\text{CeO}_2$  abrasives onto  $\text{SiO}_2$ , forming a broader adsorption layer on the silicon wafer surface [142]. Furthermore, the presence of water molecules in the environment also has an indispensable impact on the polishing of rare earth abrasives, with higher air humidity being more conducive to material removal [143].

### 2.4. Process parameters

The polishing results vary with different process parameters. Variations in abrasives, polishing slurry, grinding pressure, speed, time, polishing equipment, and polishing environment can lead to inconsistent polishing effects. The type, shape, and particle size of the abrasive also play a role in the final results. Therefore, in practical engineering, it is crucial to continually adjust and optimize these process parameters to identify the optimal combination, achieving the best polishing results to meet specific surface quality requirements for the workpiece. The summary of different polishing processes is listed in table 3.



**Figure 9.** (a) Subsurface damage change and (b) surface morphology after polishing with novel developed CMP slurry. (c) Schematic diagram of CMP mechanism for FS using two types of CMP slurries. (a)–(c) Reprinted from [99], Copyright (2023), with permission from Elsevier.

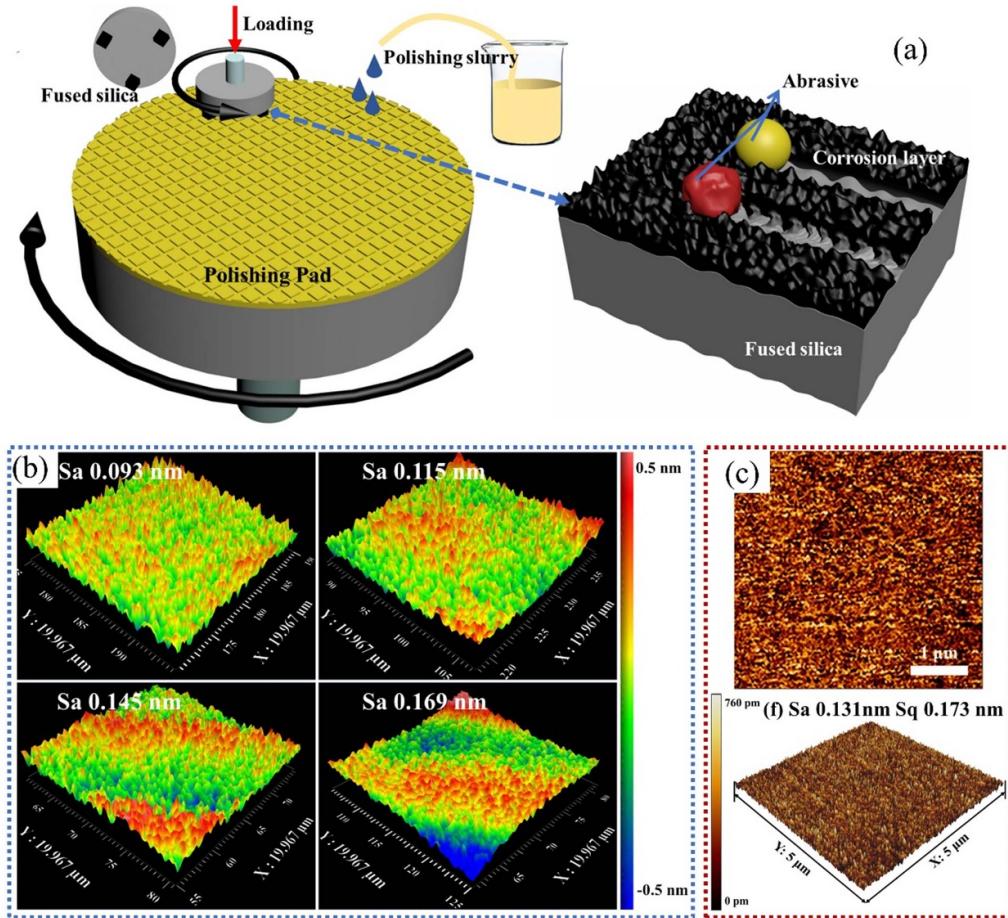
**Table 3.** Summary of different types of rare earth abrasive polishing parameters.

Polishing pressure (kPa)	Pad speed (rpm)	Slurry flow rate (ml/min)	Polishing time (min)	Polished material	Ra/Sa/Rq/Sq (nm)	Measuring range ( $\mu\text{m} \times \mu\text{m}$ )	References
27.6	50	100	5	SiO <sub>2</sub>	Ra = 0.02	$5 \times 5$	[113]
30	160	5	NA	SiO <sub>2</sub>	Sa = 0.093	$20 \times 20$	[98]
23.8	87	300	1	SiO <sub>2</sub>	Sq = 0.45	$10 \times 10$	[144]
20.7	87	120	1	SiO <sub>2</sub>	Ra = 0.183	$5 \times 5$	[145]
27.6	93	150	1	SiO <sub>2</sub>	NA	NA	[42]
200	80	NA	90	SiO <sub>2</sub>	Rq = 0.52	$5 \times 5$	[146]
20	90	100	1	SiO <sub>2</sub>	Ra = 0.36	$5 \times 5$	[147]
109.28	80	25	3	SiO <sub>2</sub>	Ra = 0.36	$5 \times 5$	[19]
27.6	40	50	0.33	STI	NA	NA	[45]
15	60	8	15	Cu	Sa = 0.099	$50 \times 50$	[140]
6.9	93	90	3	Cu	Ra = 0.363	$5 \times 5$	[106]
14.5–21.3	30–110	1.5	10	4 H-SiC	Sa = 0.084	$1 \times 1$	[148]
27.6	90	90	20	6 H-SiC	Ra = 0.11	$2 \times 2$	[101]
33	150	50	20	Al <sub>2</sub> O <sub>3</sub>	Ra = 0.52	$5 \times 5$	[74]

NA (Not available) Cu, 4 H-SiC, 6 H-SiC, Al<sub>2</sub>O<sub>3</sub> (Single crystal) SiO<sub>2</sub> (Amorphous).

The typical flat polishing device is displayed in figure 10(a). With the rotation of the polishing pad, the sample attached under the pressure plate undergoes the effects of friction with

abrasives in the polishing slurry and reacts with the chemical components in the polishing slurry. Through the combined action of these factors, the material removal effect is achieved.



**Figure 10.** (a) Schematic diagram of CMP process and abrasive scratch. (b) Surface morphology of FS after polishing using various  $\text{CeO}_2$  abrasives. (c) AFM 2D, 3D images of fused silica polished with  $\text{CeO}_2$  abrasives. (a)–(c) Reprinted from [98], Copyright (2023), with permission from Elsevier.

Recently, Xu *et al* employed a hydrothermal method to prepare nanoscale  $\text{CeO}_2$  abrasives with uniform shape [98]. The atomic force microscopy (AFM) images reveal the attainment of an atomic-scale surface with a surface roughness  $S_a$  of 0.093 nm after polishing, as depicted in figures 10(b) and (c). Their research indicates that the key to obtaining a smooth FS surface lies in the  $\equiv\text{Ce}-\text{O}-\text{Si}\equiv$  structure formed through a chemical tooth action. Several studies have demonstrated that combining thermal oxidation pretreatment with soft abrasive polishing can effectively achieve damage-free and atomically smooth polishing of the carbon surface of 4H-SiC [149]. However, it is important to note that high oxidation temperatures may result in the formation of micro-pits during the polishing process, necessitating further optimization of surface modification techniques.

When varying amounts of hydroxyl (OH) groups are introduced onto the surface of FS, the removal rate of surface atoms exhibits an initial increase with increasing hydroxylation degree, followed by a subsequent decrease. The interfacial pressure exerts influence on both the quantity and manner in which atom removal occurs. As pressure increases, the mode of removal transitions from single-atom elimination to chain

removal. This finding serves as a crucial theoretical foundation for elucidating the atomic-level mechanism underlying FS removal in CMP [150]. Zhao *et al* proposed a new cross-scale model from millimeter to nanometer scale, enabling the analysis of system logic mapping across macro, meso, micro, and nano scales. This study provides valuable insights for the design and development of CMP processes [151]. Future research should focus on exploring the potential influence mechanism of rare earth elements on CMP.

In this subsection, it can be seen that the influence of slurry compositions as well as their concentration is important to the performance of the polishing process. Rare earth abrasives like ceria mainly provided the core chemical mechanical removal mechanism and the core mechanism is very sensitive to other conditions. For examples, the change of pH and temperature would greatly promote or impede the chemical reaction, while the viscosity as well as the dispersibility of the abrasives have determined effect on the mechanical removal process. Therefore, the investment into the development of new ceria abrasives is equally important to the analysis and development of slurry composition, while the latter one is often much easier and cheaper.

### 3. Research on typical materials

Due to the special reaction mechanism between element Si and Ce, ceria abrasives have been extensively used in polishing materials with Si elements, which are mainly monocrystalline silicon, all kinds of silicate glass, FS, SiC and so on [152]. However, the material removal mechanism varies from material to material since the structure and the bond strength are very different for these materials. In this chapter, with the help of different additive in the rare earth element based polishing slurry, new polishing mechanism has been continuously reported for different materials.

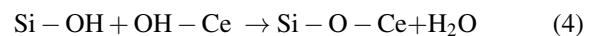
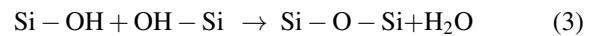
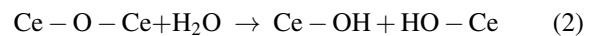
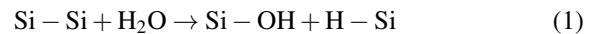
Research on different materials generally requires the adoption of specific methods to elucidate. For instance, post-polishing, material characteristics such as surface morphology, roughness, elemental composition, functional groups, and changes in molecular structure need to be investigated [153, 154]. Methods for obtaining information about material structure and elemental composition include x-ray photoelectron spectroscopy (XPS), Raman spectra, Fourier transform infrared spectroscopy (FTIR), x-ray diffractometer (XRD), energy dispersive spectrometer, and so on [155]. First principal simulation, molecular dynamic (MD) simulations are also conducted to study the material removal mechanism behind CMP [156–159]. However, there is still a big gap between macro scale polishing process and the nano scale or even atomic scale material removal process. The combination of testing like XPS, XRD and FTIR with the MD simulation is a viable solution for revealing part of the mechanism by verifying the resultant composition, there is still much to be done for revealing the mechanism.

#### 3.1. Silicon (Si)

Si is widely utilized in integrated circuits, semiconductors, and the microelectronics industry due to its narrow bandgap of 1.11 eV, intact crystal lattice structure, exceptional thermal oxidation performance, high carrier mobility, and low defect density [160–162]. As the size of silicon-based components continues to decrease, there is a corresponding increase in the surface-to-volume ratio, highlighting the growing significance of surface quality on physical and chemical properties. Consequently, precision components necessitate an ultrasmooth surface and a low-damage layer. In the Si manufacturing processes, CMP is typically chosen as a crucial step towards achieving high-quality surfaces.

In order to explore the polishing mechanism of  $\text{CeO}_2$  on the surface of Si, Cui *et al* developed a cerium dioxide-based polishing slurry [163]. After CMP, the surface is smooth, free from impurities and scratches, and the Sa measures 0.067 nm as shown in figures 11(a) and (b). The transmission electron microscopy (TEM) images in figure 11(c) reveal the effective removal of the non-uniform damage layer on the surface of single crystal silicon, leading to a significant improvement in surface quality. Moreover, a reduction in subsurface damaged layer is observed, resulting in the attainment of a sub-Ei surface for single crystal silicon. Through simulation study of the CMP mechanism (figure 11(d)), combined with experimental

results, the mechanism of the chemical reactions is shown in equations (1)–(4):

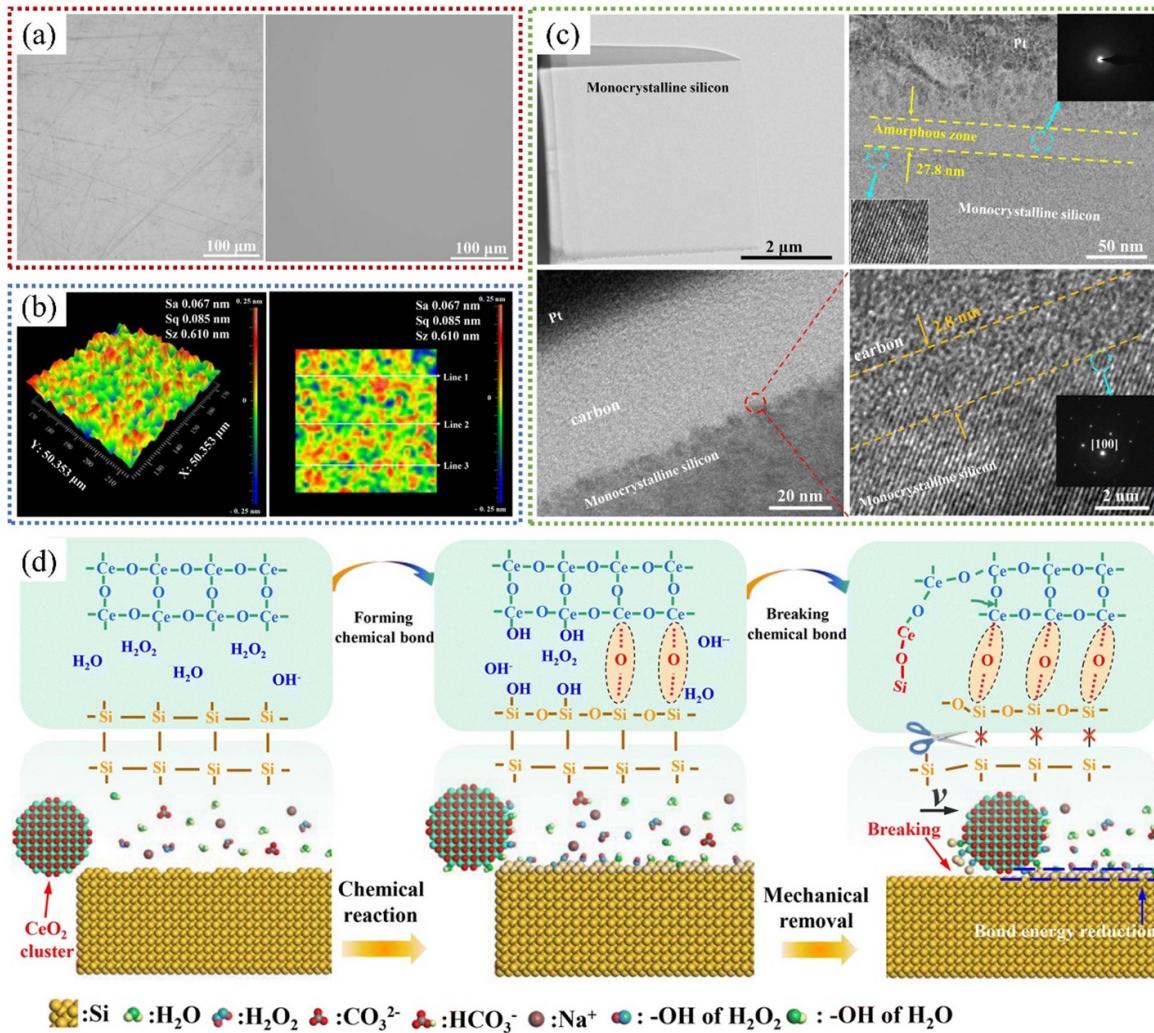


The objective of removing the surface material of silicon is achieved through the breakage of Si–O–Ce bonds. Subsequently, newly exposed silicon atoms continue to react upon contact with the polishing solution. Through this cyclic process, the removal of single-crystal silicon at the atomic level is ultimately achieved.

The mechanical removal mechanism of Si changes according to the distinct exposed surfaces of  $\text{CeO}_2$ . Some research propose that adhesive wear is the dominant form of wear between Si and  $\text{CeO}_2$ . The relationship between the friction force of Si and  $\text{CeO}_2$  is as follows:  $F(\text{CeO}_2(111)) > F(\text{CeO}_2(110)) > F(\text{CeO}_2(100))$ . The wear rate of  $\text{CeO}_2$  and its ability to remove Si during the CMP process are as follows:  $WR(\text{CeO}_2(111)) > WR(\text{CeO}_2(110)) > WR(\text{CeO}_2(100))$  and  $RR(\text{CeO}_2(111)) > RR(\text{CeO}_2(100)) > RR(\text{CeO}_2(110))$ . Consequently, it can be deduced that the  $\text{CeO}_2(111)$  surface is the predominant crystal surface prone to experiencing wear and demonstrates exceptional ability in removing Si due to its high friction force and greater hardness. Maybe because of the high surface energy, the Si removal ability of  $\text{CeO}_2(110)$  surface is poor [164]. Experiments have shown that the  $\text{CeO}_2(111)$  surface may form a greater number of Si–O–Ce bonds, while on the  $\text{CeO}_2(100)$  surface, due to lower coordination, stronger bidentate bonds with silicon can be formed by the Ce atoms. Despite having fewer Si–O–Ce bonds than the  $\text{CeO}_2(111)$  surface, the stronger bonding on the  $\text{CeO}_2(100)$  surface compensates for this and results in almost identical removal rates. This could potentially explain why practical CMP processes show higher polishing efficiency on the  $\text{CeO}_2(100)$  surface [165].

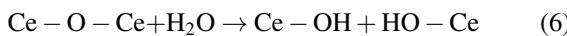
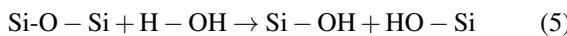
#### 3.2. FS

The CMP of silica-based glasses is a pivotal technology for achieving surface planarization and producing defect-free, ultra-smooth glass surfaces, which are indispensable for various applications including optical glasses, liquid crystal displays, display panels, window panes, precision glass lenses and glass magnetic memory disks. FS is preferred for numerous high-performance optical elements because of its exceptional optical properties and remarkable resistance to chemical, thermal, and radiation effects [166, 167]. However, its hard and brittle nature has historically limited precise machining and manufacturing processes [168]. Achieving ultra-high surface quality on FS optical surfaces efficiently remains challenging. Nevertheless, CMP technology has been employed in FS treatment, leading to significant advancements in meeting the stringent surface quality standards of FS [169]. The

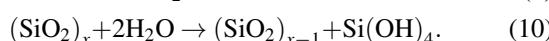
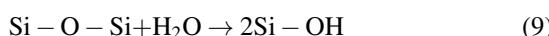


**Figure 11.** (a) SEM images of single-crystal silicon surface before and after CMP. (b) Surface roughness of the polished samples, (c) TEM images of the single-crystal silicon surface after CMP. (d) Single-crystal silicon CMP mechanism. (a)–(d) Reproduced from [163] with permission from the Royal Society of Chemistry.

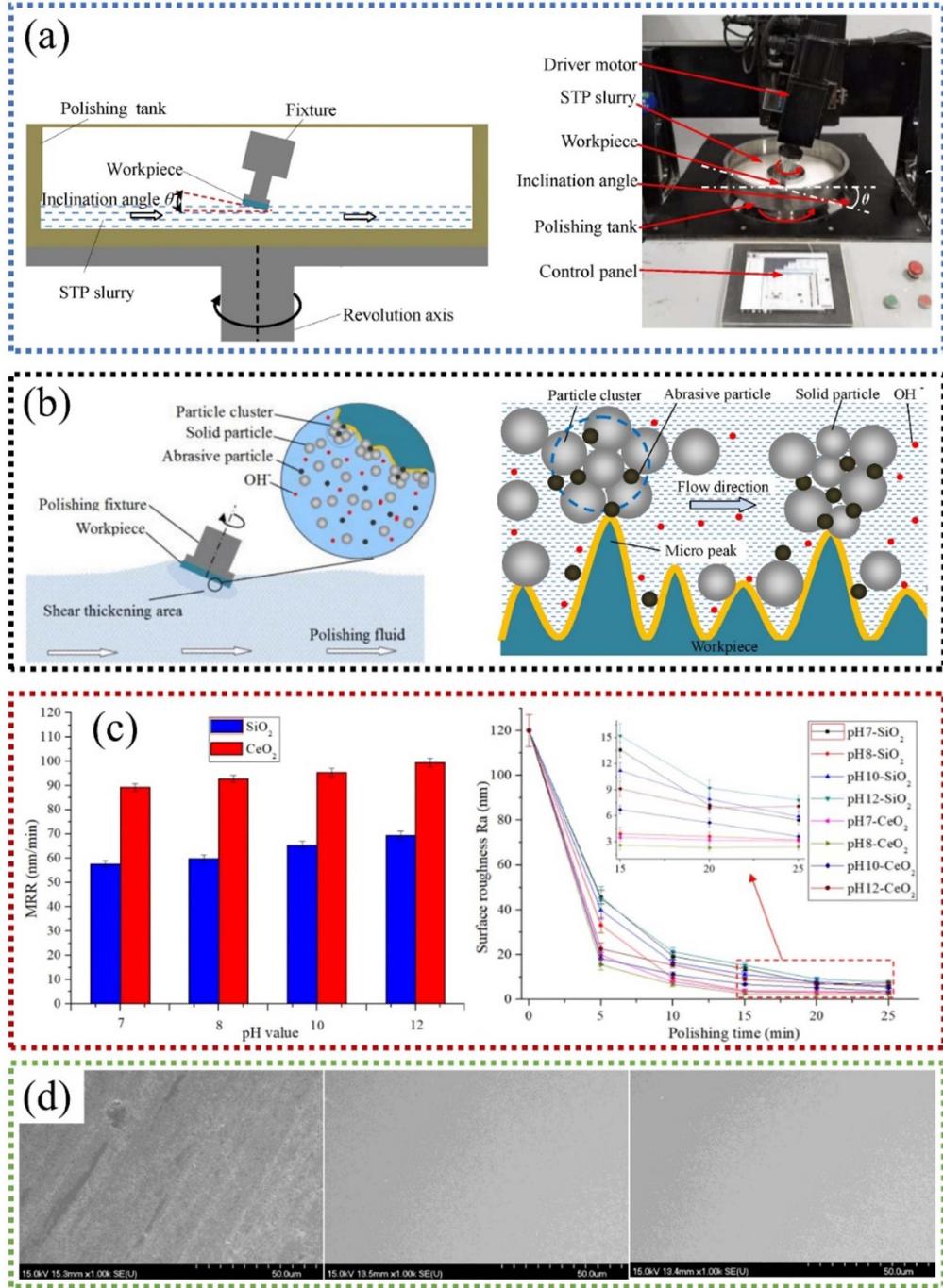
main component of FS is SiO<sub>2</sub>. When using a slurry containing CeO<sub>2</sub> abrasive for polishing the SiO<sub>2</sub> surface, the primary chemical reactions as indicated by equations (5)–(7) [50]:



In the polishing of FS glass [67–69], it has been proposed that SiO<sub>2</sub> materials may undergo hydration reactions when they come into contact with OH<sup>-</sup> in alkaline slurries [67]. XPS analyses have further confirmed the presence of Si–O, Si–O–Si, and Si–OH bonds on the surfaces of FS immersed in alkaline solutions [170]. The formation of hydration and Si–OH on SiO<sub>2</sub> surfaces as illustrated in equations (8)–(10):



At present, researchers have developed various MDs programs to simulate the CMP process. The MDs method is a key technique for studying the mechanochemical reactions of CeO<sub>2</sub> abrasives during the CMP process on SiO<sub>2</sub> surfaces [171]. A comprehensive analysis and discussion have been conducted on the atomic-level phenomena in CMP, such as bond breaking and formation, as well as the dynamics of electronic states and electron transfers. It has been discovered that the applied mechanical force significantly enhances the chemical reactions at the CeO<sub>2</sub>–SiO<sub>2</sub> interface [165]. Moreover, it is possible to observe the electron state transition from Ce<sup>4+</sup> to Ce<sup>3+</sup>. The concentration of Ce<sup>3+</sup> and oxygen exchange capacity significantly influence the polishing efficiency when using cerium-based polishing slurry for polishing SiO<sub>2</sub> [172]. Kim *et al* utilized a hydrothermal technique to synthesize ceria NPs, incorporating varying concentrations of lanthanide elements (La and Nd) as dopants in order to enhance the presence of Ce<sup>3+</sup> [59]. The incorporation of trivalent lanthanide ions into ceria induced the generation of oxygen vacancies, causing the conversion of adjacent Ce<sup>4+</sup> to Ce<sup>3+</sup> through reduction. By

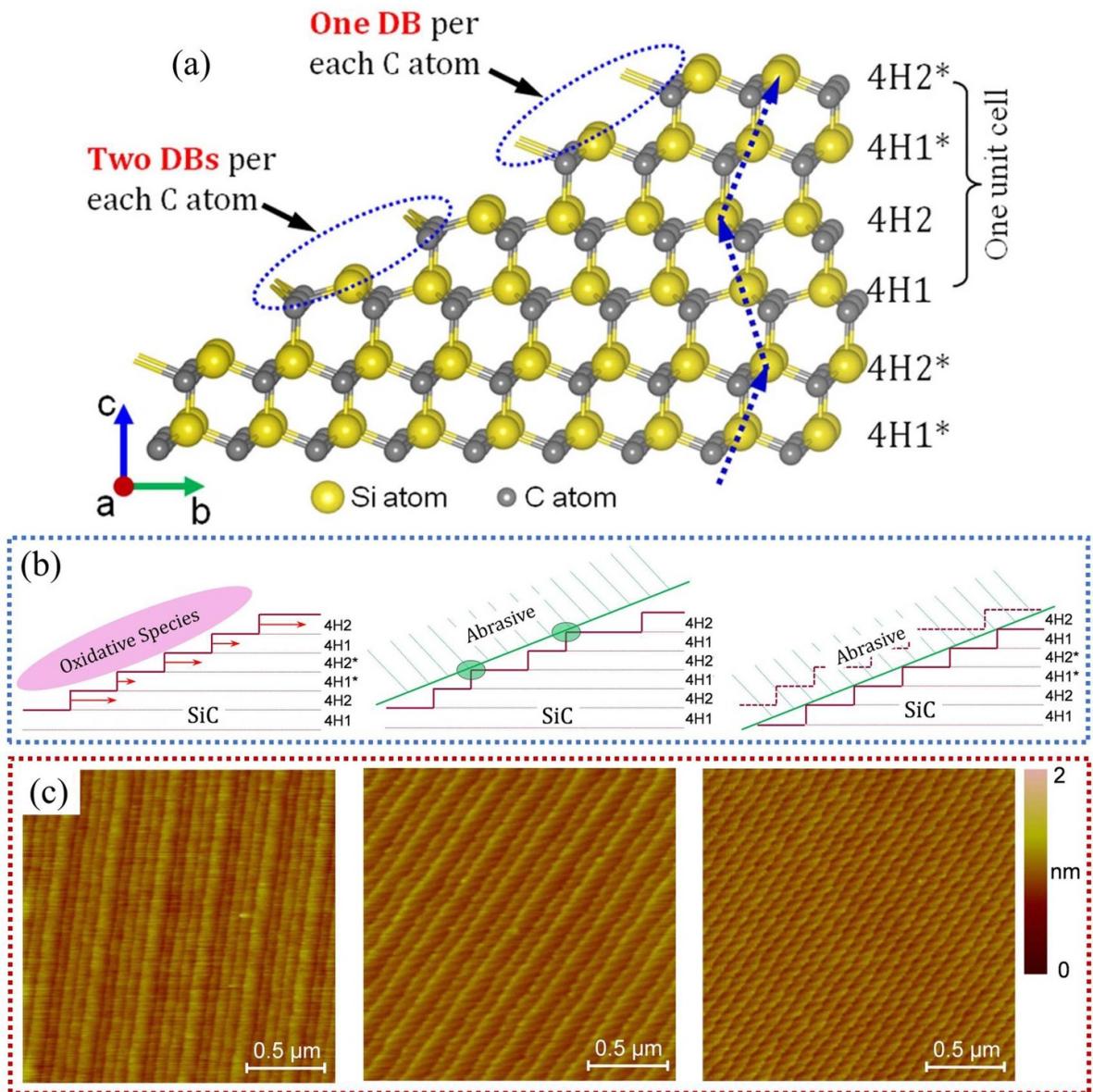


**Figure 12.** The experimental (a) device and (b) material removal mechanism schematic of the STP. (c) The variation of MRR and Ra with different pH values. (d) The surface morphology before and after polishing. (a)–(d) Reproduced from [173]. CC BY 4.0.

increasing the dopants content, particularly Nd, there was an observed increase in the concentration of  $\text{Ce}^{3+}$ . The outcomes demonstrated that La and Nd-doped cerium dioxide exhibited a remarkable MRR, indicating that elevating the concentration of  $\text{Ce}^{3+}$  can yield an exceptionally smooth  $\text{SiO}_2$  surface with a Ra value measuring 0.135 nm.

Relying on shear thickening polishing (STP) technology with non-Newtonian power-law fluids enables efficient and high-quality polishing of FS. Shao *et al* used  $\text{SiO}_2$  and colloidal  $\text{CeO}_2$  as abrasives to polish FS [173]. The experimental

device and schematic of the STP can be seen in figures 12(a) and (b), respectively. Different clamping forces are exerted on abrasives by solid abrasives at varying shear rates, significantly enhancing the force acting on them and accelerating MRR. Figure 12(c) demonstrates that increasing the pH value of the polishing slurry leads to an increase in MRR, while initially decreasing and then increasing surface roughness of FS. A preferable surface roughness is achieved when the pH value is set at 8. The surface morphology before and after polishing is depicted in figure 12(d), resulting in a decrease from



**Figure 13.** (a) Crystal structure of 4 H-SiC. (b) Generation mechanism of step-terrace structure of 4 H-SiC. (c) Variation of surface terrace-step structures of polished SiC with increasing polishing pad rotation speed by AFM. (a)–(c) Reproduced from [183]. CC BY 4.0.

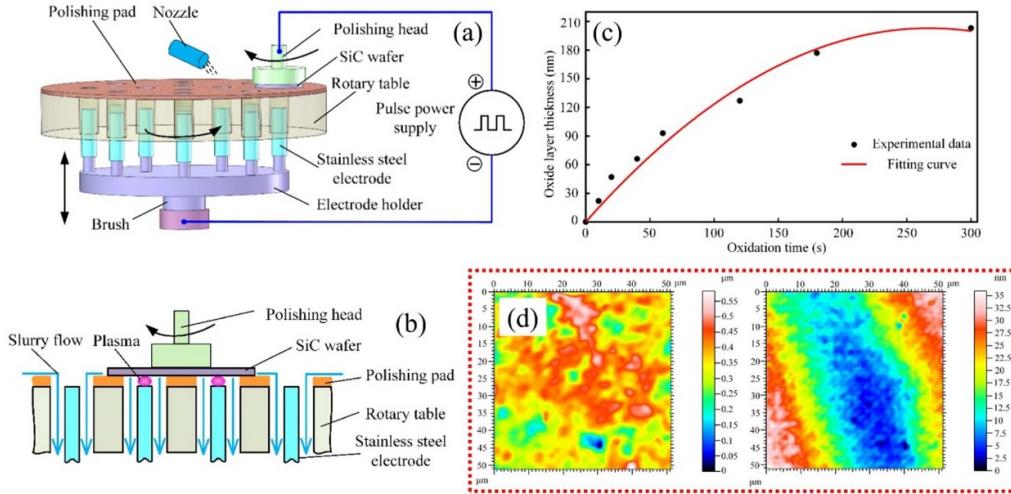
an initial Ra of  $120 \pm 10$  nm to a final Ra of 2.3 nm and 2.1 nm, accompanied by MRR values of 121.6 nm/min and 126.2 nm/min, respectively.

The esthetic appearance of all-ceramic restorations has led to their widespread utilization in dentistry. One of these materials is lithium disilicate glass ceramic ( $\text{Li}_2\text{Si}_2\text{O}_5$  or  $2\text{SiO}_2 - \text{Li}_2\text{O}$ ), with its main component being 57%–80% silica [174]. Research has revealed the presence of silica in the solution in which lithium disilicate samples are soaked. Therefore, polishing with  $\text{CeO}_2$  can be employed, where the polishing process primarily involves chemical reactions with  $\text{SiO}_2$ , ultimately yielding a smooth ceramic surface. This represents a novel approach for polishing lithium disilicate glass ceramics, pointing out a new direction for achieving atomic-level precision manufacturing of all-ceramic restorations using rare earth abrasives in the future [175].

### 3.3. Silicon carbide (SiC)

SiC has emerged as a highly promising semiconductor material for applications that require exceptional electric performance in terms of high power and high frequency. This is attributed to its outstanding characteristics, including a wide band gap, excellent thermal conductivity, high heat resistance, remarkable temperature stability, and favorable crystal lattice arrangement with GaN [176–178]. However, the challenge lies in achieving significant removal rates on the surface of SiC substrates due to their elevated mechanical hardness and pronounced chemical inertness [179–182].

The crystal structure of 4H-SiC in figure 13(a), contains four silicon–carbon bilayers in a unit cell of 4H-SiC single crystal. When polishing SiC with  $\text{CeO}_2$  slurry, as shown in figures 13(b) and (c), with the increase of polishing pad



**Figure 14.** The experimental (a) device and (b) polishing details schematic of the AOMP. (c) The change in thickness of the oxide layer over time. (d) Images of SWLI after treatment with different anodizing time and 5 min of CMP. (a)–(d) Reprinted from [184], Copyright (2020), with permission from Elsevier.

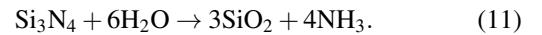
rotation speed, the stepped structure on the surface of SiC substrate changes accordingly, transitioning from the a–b–a<sup>\*</sup>–b<sup>\*</sup> type to the a–b type, and then to a uniform a–a type, presenting three structural morphologies. The MRR also increases accordingly [183].

For polishing SiC, electro CMP (ECMP) has emerged as a relatively mature technological solution, which will be elaborated on in section 4. Apart from ECMP, there are also other methods available for polishing SiC. Yin *et al* proposed a novel polishing technique that combines anodic oxidation and mechanical polishing (AOMP) [184]. Schematic diagram of the AOMP experimental device as illustrated in figures 14(a) and (b), the device comprises of an anodic oxidation system and a mechanical polishing unit, collaborating harmoniously to attain a SiC surface that is both sleek and even. The significant growth of the oxide layer during the initial phase of oxidation can be observed in figure 14(c). Subsequently, a decrease in the anodic oxidation rate leads to a reduction in the formation rate of oxide layer thickness. The impact of controlling the levels of anodic plasma oxidation rate and CMP rate was investigated to analyze their effects on polishing outcomes. Experiments showed that when the two rates were close, the minimum roughness of 1.06 nm could be obtained (figure 14(d)).

#### 3.4. Silicon nitride ( $\text{Si}_3\text{N}_4$ )

The shallow trench isolation (STI) polishing process is a specific CMP application that typically involves the selectively eliminating silicon dioxide and silicon nitride on a patterned wafer substrate [185–188]. In this scenario, the etched trenches are filled with a dielectric material (such as silicon dioxide) and polished using the silicon nitride barrier film as a stop layer. The final step of the process involves removing the silicon dioxide from the barrier film while minimizing any removal of exposed silicon nitride and trench silicon dioxide. This necessitates the use of a high selectivity slurry capable of

achieving a high relative ratio between removal rates of silicon dioxide material and silicon nitride [189–192]. Aqueous solutions readily induce  $\text{Si}_3\text{N}_4$  surface hydrolysis reactions, resulting in ammonia liberation and generation of  $\text{SiO}_2$ -like surface structures. Such hydrolysis reactions can be represented by the following equation (11).

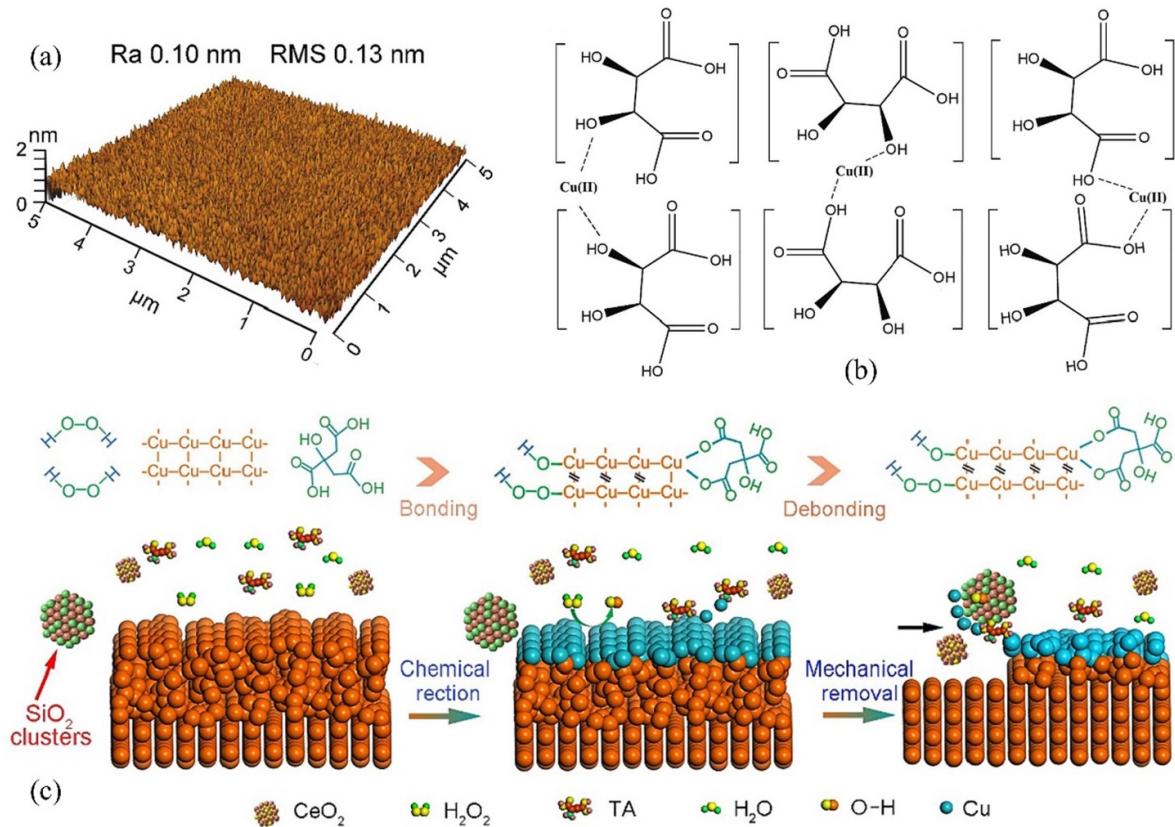


Additionally, in high-temperature environments ( $>200^\circ\text{C}$ ),  $\text{CeO}_2$  abrasives can undergo a direct chemical reaction (redox reaction) with  $\text{Si}_3\text{N}_4$  materials [193], resulting in the generation of  $\text{SiO}_2$  and  $\text{N}_2(\text{g})$ , as illustrated in equation (12). Elevating the temperature has been demonstrated to confirm that  $\text{CeO}_2$  is only stable at low temperatures [194],



when  $T > 200^\circ\text{C}$

It is discovered that the removal mechanism of polishing  $\text{Si}_3\text{N}_4$  material involves the formation of  $\text{SiO}_2$  on its surface. The  $\text{SiO}_2$  formed through further polishing eventually reaches the desired surface polishing level. When using slurry containing  $\text{CeO}_2$  abrasive for polishing STI, the diverse decomposition performance of ionic surfactants in the slurry can affect the stability of the slurry and the variation of abrasive particle size at different pH levels. Experimental results indicate that at high pH levels, the particle size distribution of  $\text{CeO}_2$  is more stable and uniform, reducing the number and depth of scratches on the surfaces of  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  during polishing [195–197]. There are studies on the impact of  $\text{CeO}_2$  abrasive particle size on STI CMP and have identified the optimal abrasive size to achieve maximum removal selectivity between oxide and nitride films, realizing atomic-level polishing of STI [198].



**Figure 15.** (a) 3D-AFM images of copper surface after CMP. (b) Chelation reaction between copper ions and tartaric acid. (c) Mechanism of copper CMP in the novel green polishing slurry. (a)–(c) Reprinted from [122], Copyright (2023), with permission from Elsevier.

### 3.5. Copper

Over the last twenty years, the CMP technique applied to copper (Cu) substrates has undergone significant evolution, transitioning from the Damascus process to the integration of barrier layers within Cu interconnects [199]. In recent years, there has been a growing consensus among researchers that surface defects and MRRs in Cu are closely tied to the properties of the polishing slurry. Consequently, considerable effort has been focused on scrutinizing the impact of various compositional factors within the slurry on Cu-CMP parameters [200].

Rare earth abrasives are applied in the precision grinding and CMP polishing of copper. Core-shell composite abrasives play a crucial role in copper CMP processes due to their unique advantages of adjustability and synergistic performance, reducing the number of deep scratches and pits caused by mechanical actions. In order to investigate the fundamental processes involved in material removal and planarization, a quantitative analysis is conducted on the nanoscratching behavior of copper film. Researchers utilized a nanoindenter system equipped with a custom-made CeO<sub>2</sub> tip, examining both constant load and ramp load modes. The detailed examination revealed that adjusting the normal force parameter and abrasive particle size can accurately predict the MRR [201]. Chen *et al* prepared polystyrene/cerium dioxide (PS/CeO<sub>2</sub>) abrasives to polish copper, achieving a surface close to an Ai-level

and proved that the potential CMP application of composite abrasives for challenging materials like copper and low-k dielectric materials [202]. SiO<sub>2</sub>/CeO<sub>2</sub> composite abrasives with different sizes of SiO<sub>2</sub> microspheres were prepared by Shi *et al* it is found that the surface roughness and MRR results are different with the change of abrasive size [106]. In traditional CMP, highly corrosive slurries such as strong acids and bases are primarily used, which can easily cause environmental pollution. Therefore, using green and eco-friendly polishing slurry to achieve atomically smooth surfaces is a major challenge currently faced. To address this issue, Liu *et al* developed a novel green CMP slurry for polishing copper surfaces [122]. They used cerium dioxide and silicon dioxide as composite abrasives, with tartaric acid serving as a pH adjuster. This approach successfully achieved a surface with a Ra of 0.1 nm, as shown in figure 15(a). The chelation product of copper ions with tartaric acid is illustrated in figure 15(b). Figure 15(c) reveals the polishing mechanism, where an adsorbed layer of copper oxides (CuO and Cu<sub>2</sub>O) and chelates forms on the copper surface and is subsequently removed. Ultimately, an atomic-level copper surface was obtained.

Oxygen-free copper (OFC) serves as a core component in high-end manufacturing with stringent surface quality requirements [203]. Achieving high-quality atomic-level surfaces has always been a significant challenge. Liu *et al* prepared well-dispersed SiO<sub>2</sub> NPs and developed a CMP slurry

composed of  $\text{SiO}_2$  NPs,  $\text{CeO}_2$  NPs,  $\text{H}_2\text{O}_2$ ,  $\text{NaHCO}_3$ , polyaspartic acid, and deionized water [105]. After CMP, the average roughness of OFC wafers reached 0.092 nm, achieving atomic-level surfaces of OFC. The present study proposes a novel approach for investigating the atomic-level polishing of Cu in future research.

### 3.6. Sapphire ( $\alpha\text{-Al}_2\text{O}_3$ ) wafer

The single crystal sapphire ( $\alpha\text{-Al}_2\text{O}_3$ ) substrate exhibits outstanding optical and mechanical characteristics, encompassing electrical and dielectric properties, hardness, and resistance to chemical corrosion [204]. Additionally, it boasts high infrared transmittance, remarkable wear resistance, and superior stability at elevated temperatures. Consequently, the use of  $\alpha\text{-Al}_2\text{O}_3$  has experienced a significant increase in cutting-edge areas like solid-state lasers, infrared windows, semiconductor chips, missile enclosures, and see-through protective shields [205]. Nevertheless, its formidable attributes, including high hardness (scoring 9 on the Mohs scale), brittleness, and chemical inertness, pose challenges in achieving sapphire wafers with the requisite surface smoothness [206]. As a crucial technique for sapphire polishing, CMP effectively regulates both the overall and localized surface smoothness during processing [207–209].

In order to delve into the polishing mechanism and interfacial contact behavior between abrasives and sapphire, Xu *et al* synthesized a novel  $\text{CeO}_2$ -coated diamond composite abrasive, which effectively reduced the surface roughness of sapphire and increased the MRR [38]. Zhou *et al* utilized PS with  $\text{CeO}_2$  and detonation nanodiamond (DND) to synthesize three types of core–shell abrasives [74]. Among them, the surface quality of sapphire polished using  $\text{PS@CeO}_2/\text{DND}$  exhibited superior characteristics. Chemical reactions inferred from the obtained XPS data are depicted as follows equations (13)–(15):



Through analysis of the polished sapphire surface and worn debris, concluded that the enhanced polishing performance is attributed to the solid-phase reaction between  $\text{CeO}_2$  and sapphire, as well as the mechanical removal effect of the composite abrasive.

From the above analysis, it can be concluded that the core chemical reaction between ceria abrasive and materials that contains Si element is the same. However, due to the different chemical activeness of other elements, the chemical reactions that happens in the polishing process as well as the final removal mechanism is vastly different. As a result, polishing slurry must be developed according to the material being polished and for difficult to machine materials like SiC and  $\text{Si}_3\text{N}_4$ , energy field assistant is often crucial for an acceptable MRR.

## 4. Rare earth abrasive energy field assisted polishing

The core concept of CMP is to first create a surface modification layer, which is softer and can be easily removed. There are many energy fields that can accelerate this process or modified the surface on their own. Therefore, energy field assistance has been considered an effective way of promoting surface quality and MRR. For decades, research have been conducted to develop novel polishing device integrates rare earth abrasives to further improve polished surface roughness and efficiency. In this section, CMP with the assistance of different types of energy fields are reviewed, including PCMP, ECMP, photoelectrochemically combined mechanical polishing (PECMP), and plasma assisted polishing (PAP). The core mechanism of these assistive technologies is briefly introduced. And the advantages and disadvantages of each assistive technology, as well as the surface quality achieved when polishing different materials with rare earth abrasives in each energy field, are summarized in table 4. It can be observed that when using rare earth abrasives as polishing abrasives, PCMP technology is primarily used for polishing  $\text{SiO}_2$ , while ECMP, PECMP, and PAP technologies are mainly used for polishing SiC. Among these, PAP technology achieves lower surface roughness for SiC. PCMP and ECMP technologies have high MRRs and polishing efficiency.

Overall, for typical materials, ECMP and PECMP typically have higher polishing efficiency, followed by PCMP, with PAP being the lowest. However, for hard materials and complex components, although PAP has lower polishing efficiency, it can achieve higher precision in surface quality. It is worth noting that introducing energy fields in the polishing process requires careful consideration of the potential environmental impacts. The leftover electrolyte from the polishing equipment in ECMP must be treated harmlessly. Comprehensive management of chemicals along with light and electrical energy in PECMP is required. Any residual gases produced by PAP equipment should be promptly treated. This is not only to prevent environmental pollution but also to ensure personal safety.

### 4.1. PCMP

PCMP technology is widely used in the ultra-precision machining of high-hardness and chemically inert materials, such as GaN and SiC, addressing the challenge of low MRRs. In PCMP [221, 222], the use of ultraviolet (UV) radiation and photocatalysts can increase the concentration of active oxygen species (such as hydroxyl radical  $\bullet\text{OH}$ , superoxide radical  $\bullet\text{O}_2^-$ ) and photogenerated holes  $\text{h}^+$  [67], as depicted in figure 16. This phenomenon accelerates the formation of the material's surface oxide layer, contributing to an improvement in MRR.

Using the same  $\text{CeO}_2$ -containing polishing slurry for CMP (without UV irradiation) and PCMP (with UV irradiation) treatment on  $\text{SiO}_2$  surfaces [69]. AFM analyses confirmed that the resulting RMS roughness values were  $0.18 \pm 0.01$  nm and  $0.17 \pm 0.01$  nm, respectively. Figures 17(a)–(c) demonstrates

**Table 4.** Comparison of different energy field-assisted polishing processes.

Polishing process	Advantages	Disadvantages	Polished material	Ra/Sa/RMS (nm)	References
PCMP	· Precise control of material removal	· Requires specialized light sources	SiO <sub>2</sub>	Ra = 0.132	[210]
	· Enhanced surface smoothness	· Limited penetration depth of UV light	SiO <sub>2</sub>	Ra = 0.137	[67]
	· Can be used on non-conductive materials	· Potential degradation of photoresist materials	SiO <sub>2</sub>	Ra = 0.12	[68]
ECMP	· High MRR	· Complex setup and control requirements	SiC	Sa = 0.853	[212]
	· Improved surface finish quality	· Potential for electrochemical corrosion	SiC	Ra = 0.51	[75]
	· Reduced mechanical stress on the workpiece	· Limited to conductive materials	SiC	Ra = 0.5	[213]
PECMP	· Combines benefits of PCMP and ECMP	· Very complex process control	SiC	Sa = 0.084	[214]
	· High precision and surface quality	· Requires both light and electrical energy sources	SiC	RMS = 0.23	[215]
	· Effective for both conductive and non-conductive materials	· Higher operational costs			
PAP	· Can process complex geometries	· Expensive equipment and operational costs	SiC	Ra = 0.277	[216]
	· Improved surface integrity and cleanliness	· Potential for surface damage due to plasma exposure	SiC	RMS = 0.3	[217]
	· high controllability	· Requires vacuum environment	SiC	RMS = 0.1	[218]
			SiC	RMS = 0.28	[219]
			SiC	RMS = 0.1	[220]

NA (Not available) RMS (Root mean square).

that both CMP and PCMP applications using these composite abrasives yielded smooth surfaces without any noticeable scratching grooves, etching pits, or residual NPs. However, cross-sectional analysis in figures 17(d)–(f) confirms that PCMP conditions contribute to reducing topographical variations, ensuring that the shape of silicon dioxide remains unchanged after polishing, enhancing shape accuracy.

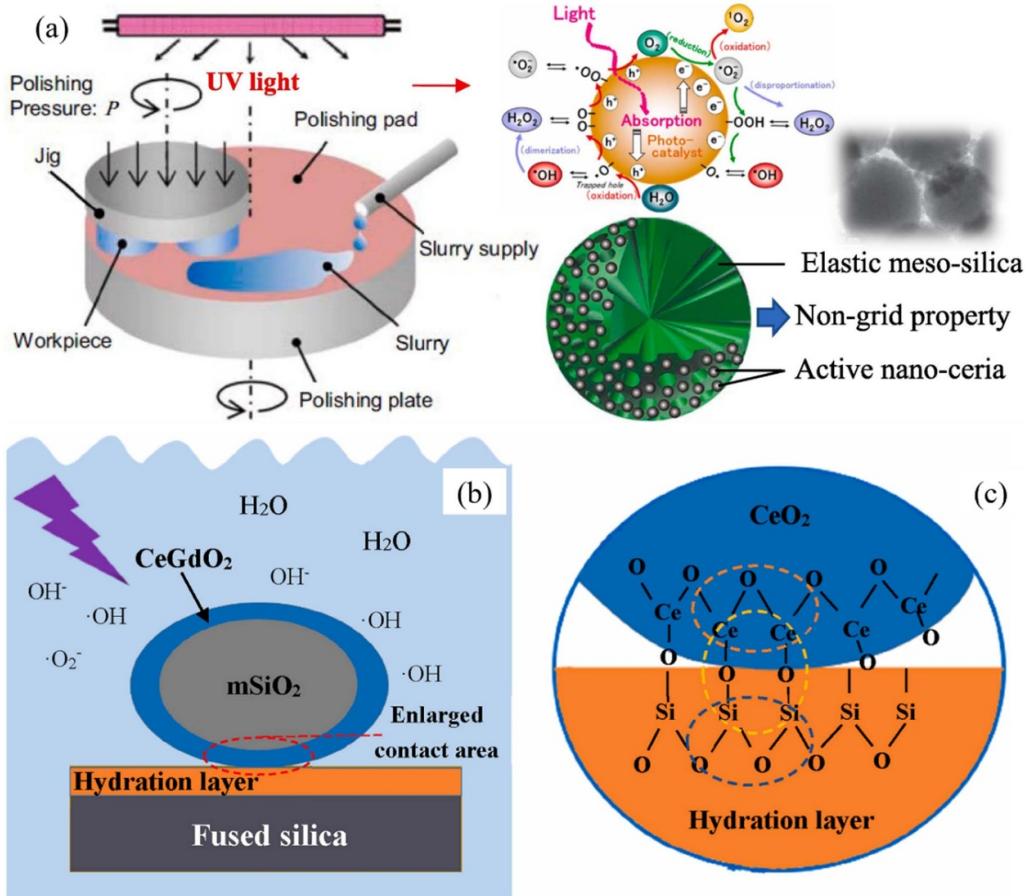
In addition to the above research, novel carbon-coupled CeO<sub>2</sub> heterostructures were developed by Wang *et al* as functional abrasives for the PCMP system [68]. As shown in the figures 18(a)–(c), surface modification occurs after the contact of CS/CeO<sub>2</sub> with oxides. The relative movement and mechanical action between the abrasive and the hydration layer cause the relatively weak Si–O–Si bonds to break, effectively removing materials during the CMP/PCMP process. From figures 18(d) and (e), it can be observed that Y-doping modification can generate more oxygen Vo and Ce<sup>3+</sup> on the surface of CeO<sub>2</sub>, as well as the effective separation of e<sup>-</sup>/h<sup>+</sup> pairs, both of which play a crucial role in enhancing photocatalytic oxidation activity.

In general, PCMP is effective in lowering the surface roughness and boosting the MRR especially for inert materials. However, the integration of the UV light into the polishing equipment is very important since the effectiveness of UV radiation on the slurry and on the polishing zone can be very different. As for the surface roughness, there is no substantial evidence that PCMP can help achieve an atomic roughness

in its current state. Therefore, it is necessary for us to further deepen our research on PCMP to achieve atomic-level manufacturing.

#### 4.2. ECMP

Recently, there has been a significant focus on enhancing the efficiency of material removal in ECMP for SiC [148, 223]. The typical experimental devices are displayed in figures 19(a) and (b) and figure 20(a). According to the findings of Murata *et al* the process of SiC wafer ECMP involves electrochemically oxidizing SiC and subsequently mechanically eliminating the resulting oxide using abrasives [75], as depicted in figure 19(c). The introduction of anodic oxidation to inert SiC has led to an enhancement in MRR. In addition, Deng *et al* employed CeO<sub>2</sub> slurry as both the electrolyte for anodizing and the polishing medium for removing the oxide layer [214]. Anodization resulted in a decrease in surface hardness from 34.5 GPa to 1.9 GPa, in accordance with figure 20(b). Surface images of the diamond-abrasive-polished surface, anodically oxidized surface, and ECMP-processed surface were presented in figures 20(c)–(e), with the ECMP-treated surface exhibiting remarkable smoothness characterized by complete elimination of all scratches and RMS roughness of 0.23 nm. Compared to the CMP process, the proposed ECMP method eliminates the need for a polishing pad, thus offering a great advantage in the process cost.



**Figure 16.** (a) Schematic images of PCMP device. (b) Interfacial contact between flexible abrasives and workpiece surfaces. (c) Tribochemical reaction between SiO<sub>2</sub> and CeO<sub>2</sub>. (a)–(c) Reprinted from [67], Copyright (2023), with permission from Elsevier.

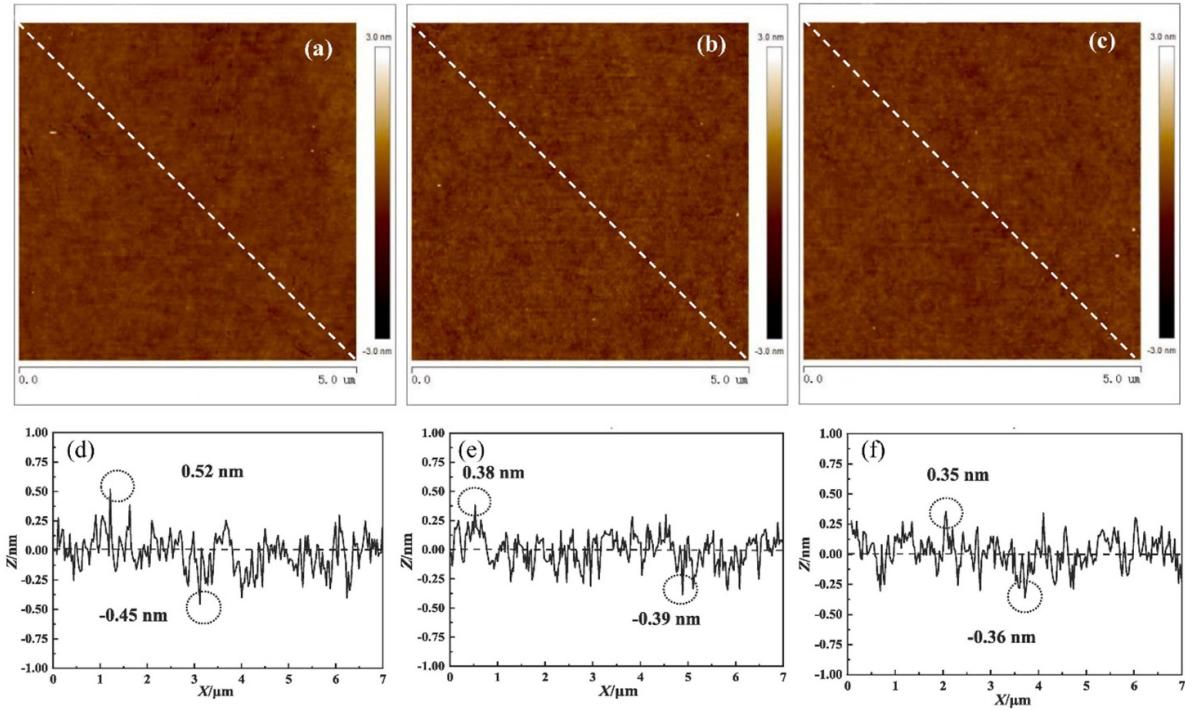
It can be concluded that ECMP is mostly for SiC or other conductive materials or semiconductors. For FS or other glasses, such method is not applicable. The surface roughness of the ECMP surface is also not desirable since the main purpose of the method is to increase the MRR. Future studies must be conducted for the possibility of achieving lower roughness.

#### 4.3. PECMP

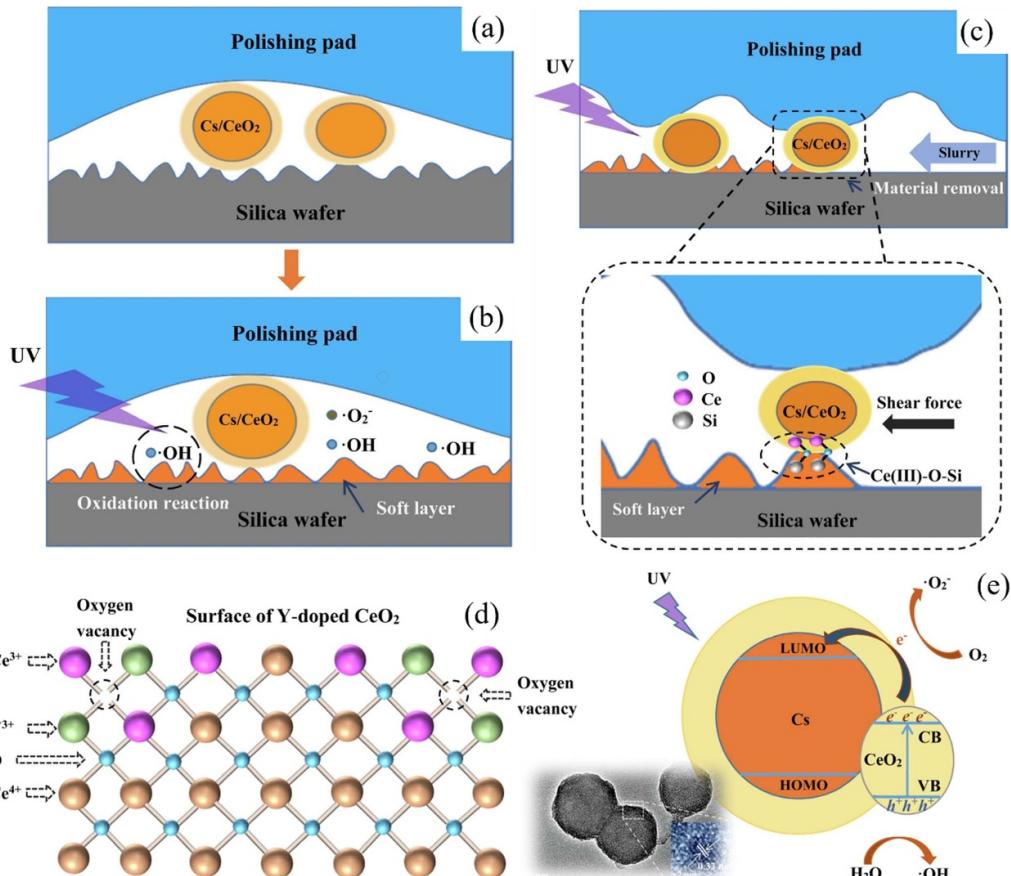
The occurrence of excessive oxidation on the SiC surface poses challenges in CMP/ECMP processes, leading to the presence of residual oxide layers and protrusions after polishing. Consequently, these protrusions made up of oxides can easily cause new scratches when they come into contact with abrasives, further deteriorating the smoothness of the polished surface. Moreover, the existing damages on the surface are exacerbated due to their inclination towards oxidation. In essence, achieving a flawless surface necessitates a significant reduction or elimination of both residual oxide layers and oxide protrusions present post-polishing [224]. To accomplish this objective effectively, it becomes imperative to maintain a controlled oxidation rate for the SiC surface. The environment-friendly PECMP technology has enormous potential for achieving ultra-precision SiC surfaces

due to the mild oxidation rate in photocatalytic reaction [225–227].

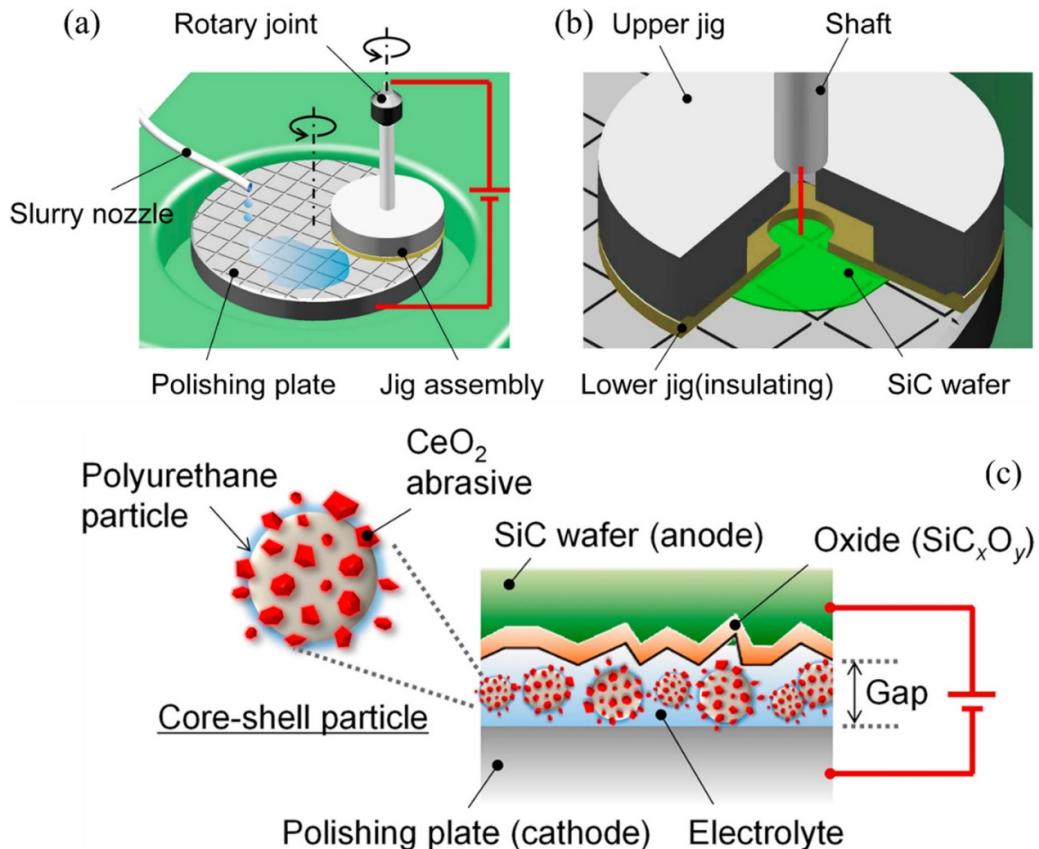
In SiC-PECMP, the material removal mechanisms [215] are as follows (figure 21). A novel technique for SiC-PECMP is depicted in figures 21(a) and (b), where a titanium mesh is utilized to immobilize PS/CeO<sub>2</sub> core/shell abrasives and CeO<sub>2</sub>–TiO<sub>2</sub> composite photocatalysts. When exposed to UV-light, electrons ( $e^-$ ) from the valence band (VB) of CeO<sub>2</sub> and TiO<sub>2</sub> will be excited and transferred to their respective conduction bands (CB), while simultaneously generating holes ( $h^+$ ) at their VBs according to equation (16). As shown in figure 21(c), the photogenerated  $e^-$  from the CeO<sub>2</sub> CB will migrate towards the TiO<sub>2</sub> CB due to its more positive potential compared to that of CeO<sub>2</sub>. Simultaneously, the photogenerated  $h^+$  from the TiO<sub>2</sub> VB will move towards the CeO<sub>2</sub> VB since its potential is more negative than that of TiO<sub>2</sub> VB. In other words, the composite CeO<sub>2</sub>–TiO<sub>2</sub> allows for a more efficient separation of electron–hole pairs during photocatalysis. When anodic bias is applied (figure 21(d)), the majority of generated electrons in the CeO<sub>2</sub>–TiO<sub>2</sub> composite film will be directed towards the Pt cathode through the external circuit. This facilitates further separation of electron–hole pairs, enhancing photocatalytic activity and significantly increasing the quantity of generated photogenerated  $h^+$ . Photogenerated  $h^+$  can oxidize



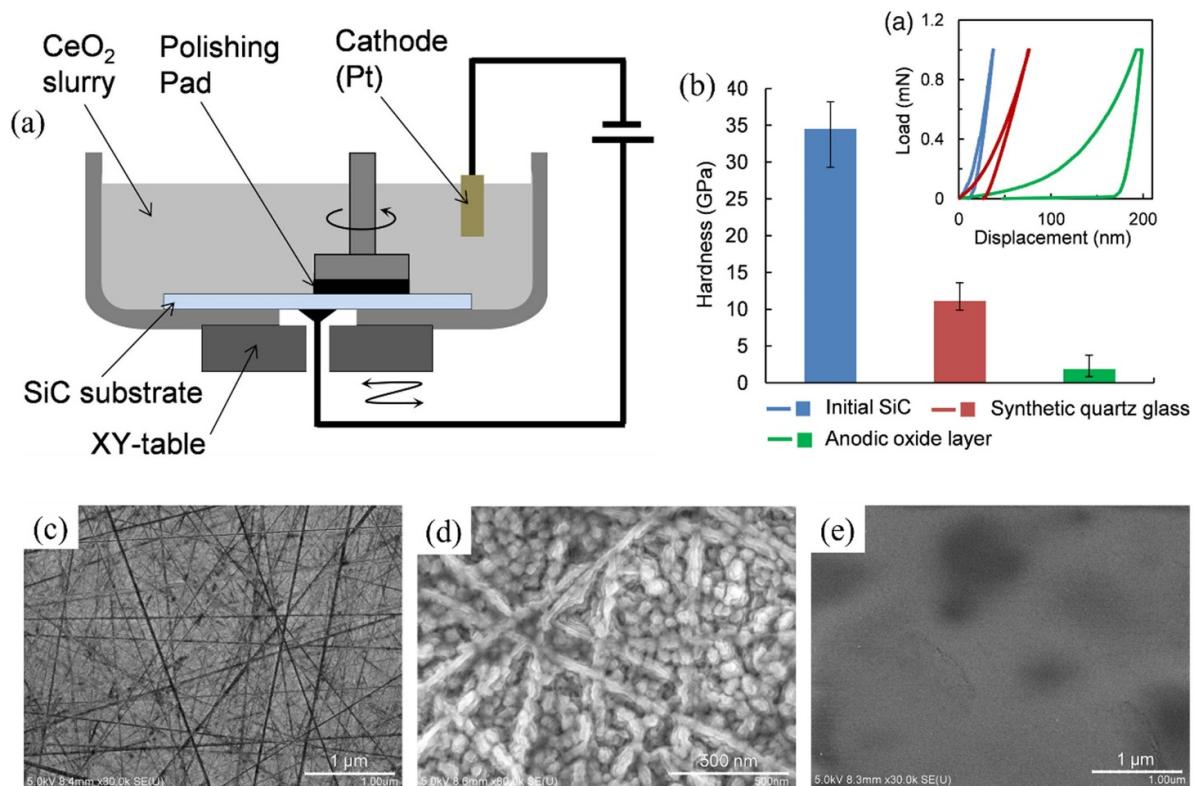
**Figure 17.** 2D-AFM images of (a) the surfaces after CMP with abrasive-A, (b) PCMP with abrasive-A, (c) PCMP with abrasive-B. Line-scan profiles of the surfaces after (d) CMP with abrasive-A, (e) PCMP with abrasive-A, and (f) PCMP with abrasive-B. (a)–(f): Reprinted from [69], Copyright (2021), with permission from Elsevier.



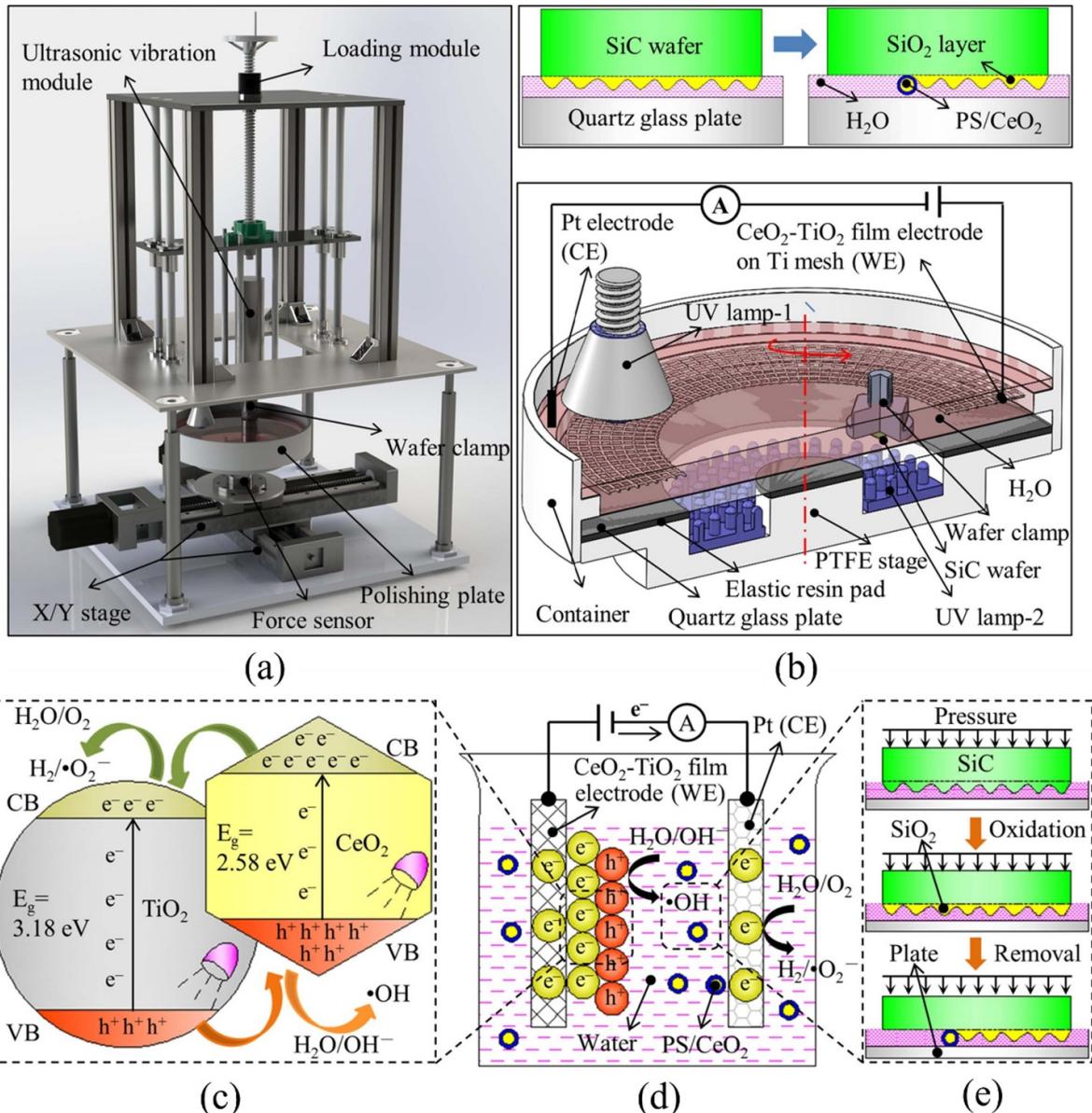
**Figure 18.** Schematics of (a) the interfacial contact, (b) the surface modification, (c) the material removal during CMP/PCMP processes using CS/CeO<sub>2</sub> functional abrasives. (d) The atomic structure of Y-doped CeO<sub>2</sub> surfaces. (e) The photooxidation mechanism toward the proposed hybrids. (a)–(e) Reprinted from [68], Copyright (2022), with permission from Elsevier.



**Figure 19.** Schematic images of (a) overall, (b) cross-sectional views of the ECMP device, and (c) the ECMP mechanism. (a)–(c) Reprinted from [75], Copyright (2017), with permission from Elsevier.

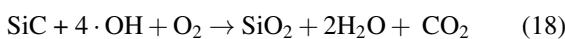


**Figure 20.** (a) Schematic images of ECMP experimental device. (b) Load-displacement curves and the hardness. SEM images of SiC surfaces after (c) diamond-abrasive-polished sample, (d) anodically oxidized sample, (e) ECMP-processed sample. (a)–(e) Reprinted from [214], Copyright (2015), with permission from Elsevier.



**Figure 21.** Schematic images of (a) PECMP device, (b) material removal process in SiC-PECMP. Mechanism of improving photocatalytic activity (c) by using a hetero structured CeO<sub>2</sub>-TiO<sub>2</sub> composite-film electrode, (d) by applying an anodic bias, and (e) material removal mechanisms in SiC-PECMP. (a)–(e) Reprinted from [215], Copyright (2021), with permission from Elsevier.

H<sub>2</sub>O into •OH (equation (17)), which subsequently oxidizes the SiC surface to form a soft SiO<sub>2</sub> layer (equation (18)). The PS/CeO<sub>2</sub> core/shell abrasives easily and gently remove this oxide layer, completely eliminating any surface damage with material removal (figure 21(e)),

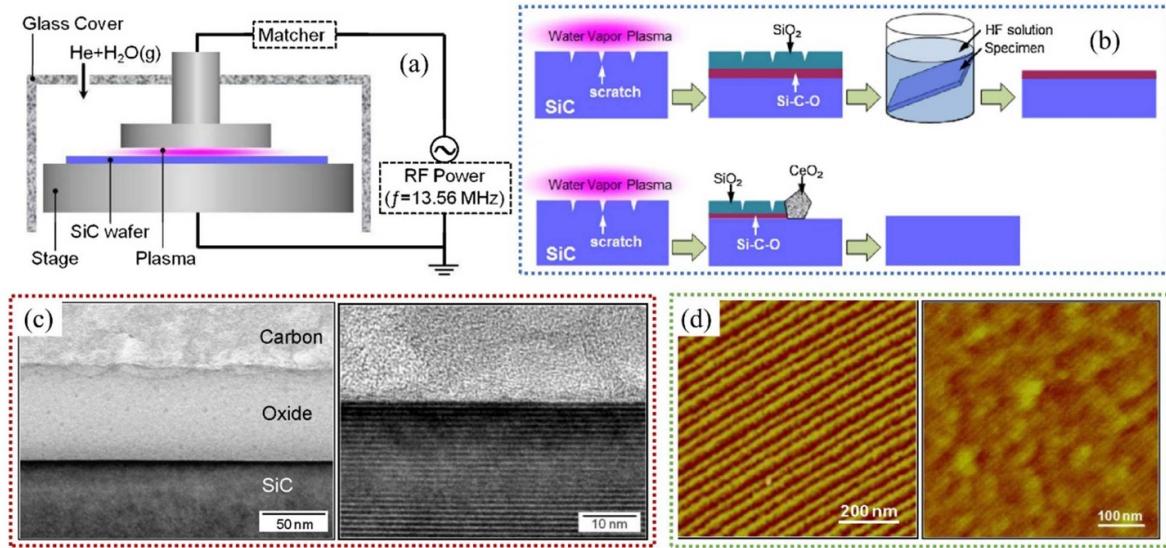


Despite the further improvement in SiC polishing efficiency through combined assistance from electric fields and ultraviolet light, the contribution of the combined effects and

coupling effects of these two energy fields remains unknown, requiring further exploration on our part.

#### 4.4. PAP

The PAP, a novel surface treatment technique that combines atmospheric pressure water vapor plasma irradiation with abrasive polishing [228–230]. The principle of PAP technology [231] is illustrated in figure 22(a). Material removal occurs primarily through two mechanisms, as shown in figure 22(b). One involves plasma oxidation and HF immersion, while the other utilizes cerium oxide abrasive within PAP. Experimental findings indicated the presence of a thin corrosion-resistant silicon oxycarbide layer at the interface



**Figure 22.** (a) Schematic images of PAP device. (b) Probable mechanism of scratch removal. (c) The XTEM and (d) AFM images of the 4 H-SiC surface before and after PAP treatment. (a)–(d) Reprinted from [231], Copyright (2013), with permission from Elsevier.

after employing the second method. The atomic plane of 4 H-SiC was achieved through a combination of steam plasma oxidation and the mechanical removal using a mild abrasive. Ultimately, this process yielded a well-ordered step/terrace morphology on the surface (figures 22(c) and (d)), devoid of any residual SiC, the surface of 4 H-SiC was successfully prepared with an RMS roughness of 0.1 nm.

## 5. Conclusion and perspectives

With the advancement of precision optics, semiconductor technology, microelectronics, and other related fields, there is a growing demand for ultra-precision atomic surfaces. Over the past decade, extensive research has been conducted on polishing media and techniques utilizing rare earth abrasives, leading to significant advancements. This paper gives a comprehensive review of the recent progress of CMP based on rare earth cerium oxide in the last two decades, including the development of new rare earth abrasives, the development of pastes, and advanced composite polishing processes for different typical materials. It can be seen from the above analysis that the surface roughness is approaching the atomic scale throughout the past decades. However, most of these works are done on small samples which can only be seen as a verification of the mechanism. And there is still a long way towards industrial application and large area atomic flatness.

In the future, the requirement of surface flatness and roughness will continue to lower, since the manufacturing accuracy and chip yield depend highly on it. Sub-2 nm chips will demand an atomic roughness, and the ultimate goal will be a surface with all atoms at the same elevation, without

any excess or absent. Rare earth abrasives have an absolute advantage in polishing silicon-containing materials due to the formation of chemical bonds during the polishing process with materials like silicon and quartz, which, through chemical mechanical action, can achieve atomic-level surface processing. However, because rare earth abrasives are softer compared to other commonly used abrasives like  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , they are generally not suitable for polishing metals, metal oxides, and composite materials, which are non-silicon-based. Additionally, while rare earth composite abrasives and core-shell abrasives are effective, they are difficult to produce and expensive, further limiting the widespread application of rare earth abrasives in CMP. Therefore, future efforts should focus on simplifying the synthesis steps of rare earth abrasives, reducing synthesis costs, and producing rare earth abrasives with strong universality.

It is difficult to control the scratch depth of abrasives on the material surface uniformly in traditional CMP. To achieve an ideal smooth surface, additional physical fields must be incorporated to effectively lower the material removal volume per scratch to atomic scale. For example, laser-assisted or ultrasonic vibration-assisted polishing has been proven effective in reducing surface roughness and improving the MRR. However, since planar polishing involves securing the material between the polishing pad and the platen, integrating these energy fields into the polishing process poses a challenge for the design and development of polishing equipment. If the surface modification can be controlled to the atomic scale, while the material removal process be achieved by controllable load like nanometric vibration instead of abrasive movements, an atomic roughness can be achieved. In terms of lowering the material removal depth for each abrasive to slowly achieve the atomic roughness, the concept of removing a single layer of

atoms has been proven by previous works. In the atomic and close to atomic scale manufacturing field, it was revealed that the material removal mechanism transforms from cutting to ploughing and to pushing when the cutting depth approaches the atomic scale. But in a latest study, an atomic scale cutting phenomenon which captures the atoms after immediate elastic recovery state and achieve a cutting action at the scale of three to four atoms deep. Such phenomena shows that there are still a lot of unknown mechanism at the atomic scale for achieving atomic roughness.

## Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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